

(19)



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(11)

**EP 1 106 348 B1**

(12)

**EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the grant of the patent:  
**10.09.2003 Bulletin 2003/37**

(51) Int Cl.7: **B41C 1/10, B41M 5/36**

(21) Application number: **00126519.8**

(22) Date of filing: **08.12.2000**

(54) **Planographic printing plate precursor**

Flachdruckplattenvorstufe

Précurseur de plaque d'impression planographique

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE TR**

(30) Priority: **10.12.1999 JP 35221099**

(43) Date of publication of application:  
**13.06.2001 Bulletin 2001/24**

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(56) References cited:  
**EP-A- 0 819 985 EP-A- 0 864 420**  
**EP-A- 0 881 096 EP-A- 0 908 779**  
**EP-A- 0 914 941**

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**Description****BACKGROUND OF THE INVENTION**5 **Field of Invention**

**[0001]** The present invention relates to a plate for planographic printing with which direct plate formation, in which a plate can be formed directly by scanning an infrared laser based on digital signals from a computer or the like, is possible. Specifically, the present invention relates to an infrared-sensitive planographic printing plate suitable for alkali  
10 developing processing.

**Description of the Related Art**

**[0002]** High-output, compact solid-state lasers, semiconductor lasers, and gas lasers, which emit ultraviolet light, visible light, and infrared light having wavelengths ranging from 300nm to 1200nm, have become readily available. These lasers are very useful as a recording light source for making a printing plate directly from digital data of computers or the like.

**[0003]** Various studies concerning recording materials sensitive to these various types of laser have been made. Typical examples of recording materials that can be recorded by an infrared laser beam having a wavelength of 760nm or greater include the positive-type recording material described in U.S. Patent No. 4,708,925, and the negative-type recording material that is crosslinkable by an acid catalyst and described in Japanese Patent Application Laid-Open (JP-A) No. 8-276558.

**[0004]** Examples of recording materials responsive to an ultraviolet or visible light laser having a wavelength of 300nm to 700nm are numerous, and include the radical polymerizable, negative-type recording materials disclosed in  
25 U.S. Patent No. 2850445 and Japanese Patent Application Bulletin (JP-B) No. 44-20189.

**[0005]** In the greater part of such image recording materials that use various kinds of laser beams, particularly in drawing techniques which use an infrared laser having a wavelength of 760nm or greater, an image is formed by using high heat generated at portions irradiated with the infrared laser. Because the high heat used in this manner is utilized not as an optical mode but as a heat mode, a threshold property appears in image formation and a very contrasty image quality is obtained, so that such image recording materials are preferable as printing materials. To briefly describe threshold property in image formation, in the optical mode, when unexposed portions are irradiated only with weak light leaked at the exposure apparatus, photochemical reactions and the like corresponding to the amount of leaked light are generated, whereby fogging is produced. By contrast, in the heat mode, because a high temperature is not generated unless an amount of light greater than a given value is irradiated, a thermal reaction is not generated (threshold property) and fogging at weakly exposed regions is not produced. On the other hand, at exposed portions irradiated with a strong light, a high temperature is generated and a sufficient image is formed, even in the heat mode. The result is a contrasty image.

**[0006]** Ordinarily, when used as a heat mode characteristic, and in particular when used as material for a printing plate, a support made of metal such as aluminum is used from the standpoint of printability, smoothness and processing ease. However, there is the drawback that heat diffuses from the support and exposure energy is not used effectively for recording, thus leading to a considerable drop in sensitivity.

**[0007]** For this reason, the use of an insulated support or the provision of a heat-insulating material on a support are effective when an image is formed in the heat mode. Because sensitivity is greatly improved by the effect of preventing heat diffusion caused by a reduction in heat conductivity, various insulation methods have been explored.

**[0008]** However, one of the large characteristics of a printing plate is that it is structured by an image portion (a region that is highly hydrophobic and whose affinity to ink is high) and a non-image portion (a region that is highly hydrophilic and ink-repellant). Here, when a highly hydrophobic material is used as a heat insulating material, the non-image portion (highly hydrophilic portion) must be formed by exposure in order to actually function as a printing plate. When the hydrophilic portion is not formed sufficiently, it becomes easy for ink to adhere to areas whose hydrophilicity has been lowered by abrasion at the time of printing, and there emerges the possibility for contamination in printing to occur.

**[0009]** Conversely, when a highly hydrophilic material is used as a heat insulating material, when the image portion (highly hydrophobic portion) is formed by exposure, problems arise in that damping water at the time of printing penetrates the surface of the heat insulating material along the hydrophilic portion thereof, whereby the photosensitive layer is stripped away by surface destruction, thus leading to a deterioration in printability.

**[0010]** As examples of a structure in which such problems originating in heat insulating materials are few, systems which utilize a heat insulating material at the support or in the vicinity thereof and which carry out recording by ablation, which are systems without alkali developing processing (hydrophilic processing), and systems in which a hydrophilic region and a hydrophobic region are formed in the surface by a polar-transformable material have been investigated.

When recording is conducted using ablation, recording layer material is scattered within the exposure apparatus, whereby particularly delicate lenses in a laser transmission section are contaminated. For that reason, there has been the need to additionally furnish a device to remove the ablated materials. The apparatus thus grows complex and is not desirable in terms of costs. Raising printability is therefore substantially difficult in view of the present circumstances.

[0011] There are no problems associated with contamination of optical systems when polar-transformable materials are used. However, because the hydrophobic regions are formed by utilizing only polar variations in the vicinity of the surface of the printing plate, repeated printings of 300,000 plates or more cannot possibly be withstood, printability is low, and there is the fear that contamination in printing caused by a deterioration in the hydrophilicity of the non-image portion will occur.

[0012] Accordingly, attempts have been made to develop a heat insulating technology that will eliminate problems associated with heat loss, without adversely effecting other characteristics required of a planographic printing plate, such as compatability with ink used in printing, printability, adhesion to the recording layer, and the like.

[0013] EP 0 914 941 A1 relates to a method to making positive working printing plates comprising the steps of

a exposing imagewise to IR Radiation a heat mode imaging element having on a lithographic base with a hydrophilic surface layer including a polymer, soluble in an aqueous alkaline solution and a top layer provided thereon which contains a compound capable of converting light into heat.

b developing said imagewise exposed element with an alkaline developer whereby the exposed areas of the first and the top layer are dissolved and the unexposed area of the first layer remain undissolved.

[0014] EP 0 908 779 A1 discloses a method for making a positive working printing plate which comprises the above steps a and b characterised in that the top layer includes an organic quaternary ammonium salt.

[0015] EP 0 881 096 A1 provides a heat sensitive imaging element comprising

a a lithographic base with a hydrophilic surface

b an image forming layer including a hydrophobic thermoplastic polymer latex and

c a compound capable of converting light into heat, being present in said image forming layer or a layer adjacent thereto, characterised in that the heat-sensitive imaging element comprises

d a barrier layer between the lithographic base and the image-forming layer, said barrier layer and said image-forming layer being removable in an aqueous solution with a pH of at least 5.

[0016] EP 0 864 420 A1 describes a heat sensitive-imaging element for making positive working lithographic printing plates comprising

a on a lithographic base

b a layer comprising a polymer, soluble in an aqueous alkaline solution

c and an IR radiation sensitive top layer.

[0017] Upon imagewise exposure the capacity of the aqueous alkaline solution to penetrate and/or solubilise the top layer is changed.

[0018] EP 0 819 985 A1 relates to a radiation sensitive imaging element comprising on a hydrophilic surface of a lithographic base an image-forming layer comprising an alkali soluble or swellable resin having a phenolic hydroxy group, a latent Bronsted acid and an infra-red absorber, characterised in that said image-forming layer comprises an amino crosslinking agent.

## SUMMARY OF THE INVENTION

[0019] An object of the present invention is to improve the loss of exposure energy and to form an image in which the on-off thereof in the irradiated and non-irradiated portions is enlarged in an infrared-sensitive planographic printing plate and to provide an aqueous alkali developing type planographic printing plate having high sensitivity and high printing durability.

[0020] The inventors of the present invention have conducted various studies to solve the aforementioned problem

and, as a result, found that the drop of the heat of a recording layer is prevented and a hydrophilic/hydrophobic region is formed without decreasing adhesion between a support and a recording layer, for example, by using a material having low thermal conductivity and by providing a layer having the ability to make the surface thereof hydrophilic by using an alkali developing solution or by using a support which itself has such an ability. The present invention was thus completed.

**[0021]** Accordingly, the planographic printing plate of the present invention comprises forming a first layer which is made of an heat-insulating material having a low thermal conductivity and is made hydrophilic by treating using an alkali or a silicate in an alkali developing solution after being exposed and a second layer which is an infrared ray-sensitive recording layer to be changed in alkali developing ability without being abraded by irradiation with infrared rays in this order on a support, said IR-sensitive layer being a negative type radical polymerization layer.

**[0022]** Also, in one embodiment, the planographic printing plate of the present invention uses, as the support, a material made of a low heat-conductive insulating material and having the ability to make the surface thereof hydrophilic by treating using an alkali or a silicate in an alkali developing solution after being exposed and an infrared-sensitive layer which is changed in alkali developing ability by irradiation with infrared rays is disposed on the support, said IR-sensitive layer being a negative type radical polymerization layer.

**[0023]** Here, the thermal conductivity of the above heat-insulating material is  $3.0 \text{ (W} \cdot \text{m}^{-1} \cdot \text{K}^{-1})$  or less and preferably  $1.0 \text{ (W} \cdot \text{m}^{-1} \cdot \text{K}^{-1})$  or less.

**[0024]** Also, the layer made of a heat-insulating material and provided with a surface to be made hydrophilic preferably has an average thickness ranging from  $0.05$  to  $50 \text{ }\mu\text{m}$ , in particular from  $0.2$  to  $50 \mu\text{m}$ . When such a heat-insulating material is used as the support itself, the average thickness of the heat-insulating material is preferably in a range from  $0.05$  to  $5.0 \text{ mm}$ , in particular from  $0.05$  to  $2.0 \text{ mm}$ .

**[0025]** The planographic printing plate of the present invention uses a heat-insulating material having such a hydrophilic level as to enable the light-sensitive layer to adhere as the support itself or as the layer disposed between the support and the light-sensitive layer (recording layer). Also, the heat-insulating material having such a property as to enable only the unexposed portion to be made hydrophilic after the surface is exposed by an infrared laser is used. Therefore, the image portion is not made hydrophilic so that adhesion to the recording layer is secured. At the same time, in the non-image portion, the surface of the heat-insulating material acquires hydrophilicity for the first time by performing alkali developing processing (hydrophilicity treatment) in an alkali development treating step. The present invention enables the preparation of a planographic printing plate which attains high sensitization using a heat insulating material, is freed of the penetration of an alkali developing solution between the recording layer and the support, has clear on-off of an image portion/a non-image portion and is superior in printing durability.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

**[0026]** An infrared-sensitive planographic printing plate of the present invention will hereinafter be described in detail.

**[0027]** The planographic printing plate of the present invention may have a layer (appropriately termed a "heat-insulating intermediate layer" hereinafter), disposed between a support and an infrared-sensitive recording layer, structured by a heat-insulating material having a low thermal conductivity, and that is made hydrophilic by being treated with an alkali or a silicate in an alkali developing solution after exposure. Said IR sensitive layer is a negative-type radical polymerization layer. Alternatively, the planographic printing plate of the present invention may have a support (appropriately termed a "heat-insulating support" hereinafter) formed of a heat-insulating material having a low thermal conductivity, with the support having a surface that is made hydrophilic by being treated with an alkali or a silicate in an alkali developing solution after exposure.

**[0028]** When the heat-insulating intermediate layer is provided on the support, the heat-insulating material of the heat-sensitive planographic printing plate of the present invention preferably uses materials that have a cross-linkable structure, from the standpoint of abrasion at the time of printing. Further, the heat-insulating intermediate layer changes to a hydrophilic layer that is essentially ink-repellant by the action of an alkali or a silicate in an alkali developing solution at the time of alkali developing processing.

**[0029]** On the other hand, when the heat-insulating support which itself is the heat-insulating material is used, the surface thereof must be provided with surface treatment enabling the surface to be changed to an ink-repellent hydrophilic surface during the above alkali developing processing. As this surface treatment, a method of forming the surface treated layer unitedly on the above heat-insulating support is preferably used.

**[0030]** The thermal conductivity of the heat-insulating material used here is  $3.0 \text{ (W} \cdot \text{m}^{-1} \cdot \text{K}^{-1})$  or less and preferably  $1.0 \text{ (W} \cdot \text{m}^{-1} \cdot \text{K}^{-1})$  or less.

**[0031]** When the heat-insulating material is used as the heat-insulating intermediate layer, the average thickness of the heat-insulating layer is in a range of  $0.05$  to  $50 \mu\text{m}$ , preferably  $0.1$  to  $10 \mu\text{m}$  and most preferably  $0.2$  to  $5.0 \mu\text{m}$ . When the thickness is less than  $0.05 \mu\text{m}$ , the effect of insulation significantly decreases. When the thickness exceeds  $50 \mu\text{m}$ , the possibility of the surface being stripped away from the support at the time of printing increases. When the heat-

insulating support is used, the thickness thereof is in a range of 0.05 to 5.0 mm and preferably 0.05 to 2.0 mm. When the thickness is less than 0.05 mm, dimensional accuracy becomes poor, causing printing displacement. On the other hand, when the thickness exceeds 5.0 mm, the support cannot withstand flexural strength when it is wound around a printer, causing cracks in the support itself.

5 The heat-insulating material used as the heat-insulating intermediate layer in the planographic printing plate of the present invention must be, first, a material whose thermal conductivity is low. Second, it is necessary that the heat-insulating material has good adhesion to the photosensitive layer, has a surface that is hydrophobic or weakly hydrophilic at least to the extent that ink adheres, and that is made substantially hydrophilic by the alkali developing processing to the extent that the material repels ink.

10 **[0032]** Preferable examples of materials that fulfill such requirements include vitreous inorganic compounds, inorganic/organic hybrid compounds, and organic polymer compounds. A material containing air therein, such as foamed styrol, is also preferable. From the standpoint of being made hydrophilic by the alkali developing processing, it is essential that the heat-insulating material has a compound, particularly a polymer organic or inorganic compound, having a hydroxyl group, a primary amino group, a secondary amino group, an acid group (particularly, a phenol group, 15 an imide group, a sulfonamide group, a mercapto group, a carboxylic acid group, a sulfonic acid group, a phosphoric acid group, a phosphonic acid group and a silicic acid group) or an acid group precursor (particularly, alkylesters, arylesters, acid anhydrides or acid halides), which are functional groups that become hydrophilic or whose hydrophilicity is strengthened when the groups react with an alkali or a silicate in a developing solution.

**[0033]** For the formation of such heat-insulating intermediate layer which can be made hydrophilic, conventionally 20 known, crosslinked hydrophilic layer technology may be applied.

**[0034]** Crosslinked hydrophilic layer technology can be utilized because of the advantages that a strong film can be formed because much of the technology includes functional groups made hydrophilic by the aforementioned alkali developing treatment.

**[0035]** Any one of conventionally known, cross-linked hydrophilic layers may be used as such a cross-linkable hydrophilic layer. For example, 1) the hydrophilic layer formed of a crosslinked polymer having a metal colloid as disclosed 25 in International Application Laid-Open W098/40212, 2) the hydrophilic layer formed of a condensate of an organic hydrophilic polymer and a silane coupling agent as disclosed in Japanese Patent No. 2592225, or 3) the hydrophilic layers formed of a crosslinked organic polymer as disclosed in Japanese Patent Application Laid-Open (JP-A) No. 10-6468 and Japanese Patent Application Laid-Open (JP-A) No. 10-58636 may be used.

30 **[0036]** The crosslinked hydrophilic layers will hereinafter be described sequentially.

**[0037]** First, 1) the hydrophilic layer formed of a crosslinked polymer having a metal colloid will be described.

**[0038]** Examples of the metal colloid include colloids of hydroxysilane, hydroxyaluminum, hydroxytitanium and hydroxyzirconium. These metal colloids may be crosslinked using a crosslinking agent such as a di-, tri- or tetraalkoxysilane, titanate or aluminate to form a polymer. The metal colloid may be produced according to USP2,244,325 or 35 USP2,574,902. Among the above metal colloids and crosslinking agents, a particularly useful metal colloid is colloidal silica and a particularly useful crosslinking agent is aminopropyltriethoxysilane. The amount of the metal colloid to be used is in a range of 100 to 5000% and preferably 500 to 1500% with respect to the amount of the crosslinking agent.

**[0039]** Next, 2) the hydrophilic layer formed of a condensate of an organic hydrophilic polymer and a silane coupling agent will be described.

40 **[0040]** For instance, it is preferable to cast a hydrophilic polymer having a free reactive group such as hydroxyl, carboxyl, hydroxyethyl, hydroxy-propyl, amino, aminoethyl, aminopropyl or carboxymethyl group from an aqueous composition containing a suitable crosslinking agent or modifying agent containing, for example, a hydrophilic organic titanium reagent, aluminofornyl acetate, dimethylolurea, melamine, aldehyde or hydrolyzed tetraalkyl orthosilicate.

**[0041]** The polymer suitable to form the above hydrophilic layer may be selected from a group of gum arabic, casein, 45 gelatin, derivatives of starch, carboxymethyl cellulose and Na salts thereof, cellulose acetate, sodium alginate, vinyl acetate/maleic acid copolymers, styrene/maleic acid copolymers, polyacrylic acids and salts thereof, polymethacrylic acids and salts thereof, hydroxy-ethylene polymers, polyethylene glycols, hydroxypropylene polymers, polyvinyl alcohols and hydrolyzed polyvinyl acetate of which the degree of hydrolysis is at least 60 wt% and preferably at least 80 wt%.

**[0042]** Specifically, the hydrophilic layer disclosed in USP 3,476,937 is particularly preferable because it produces 50 excellent lithographic printability when used as the planographic printing plate of the present invention. This hydrophilic layer has polyvinyl alcohol or polyvinyl acetate that has been hydrolyzed at least to 60wt.%, and the hydrophilic layer is film-hardened by a tetraalkyl orthosilicate such as tetraethyl orthosilicate or tetramethyl orthosilicate.

**[0043]** Another suitable film-hardened hydrophilic surface layer is disclosed in EP-A-0 514 990. The hydrophilic layer disclosed in this European Patent has a copolymer (e.g., amino modified dextran), which contains an amine or amide 55 functional group having at least one free hydrogen, and a hardened reaction product of an aldehyde.

**[0044]** When this film-hardened hydrophilic surface layer is used as the heat-insulating intermediate layer in the planographic printing plate of the present invention, additional materials such as plasticizers, pigments and dyes may be included to improve the qualities of the layer. Specifically, particle materials such as TiO<sub>2</sub> or colloidal silica may also

be included to improve the strength and/or hydrophilicity of the layer. Next, 3) the hydrophilic layer formed of a crosslinked organic polymer will be explained.

**[0045]** The crosslinked organic polymer in the present invention may be a networked polymer, structured from carbon-carbon bonds, having as side chains thereof one or more types and a plurality of hydrophilic functional groups such as a carboxyl group, an amino group, a phosphoric acid group, a sulfonic acid group, salts of these groups, a hydroxyl group, an amide group, a polyoxyethylene group or the like. The crosslinked organic polymer may also be a polymer in which one of carbon atoms and carbon-carbon bonds are connected by hetero atoms formed of at least one type or more of oxygen, nitrogen, sulfur or phosphorous. The crosslinked organic polymer may also be a networked polymer having as side chains thereof one or more types and a plurality of hydrophilic functional groups such as a carboxylic group, an amino group, a phosphoric acid group, a sulfonic acid group, salts of these groups, a hydroxyl group, an amide group or a polyoxyethylene group. Specific examples of these organic polymers may include polymers such as poly(meth)acrylate types, polyoxyalkylene types, polyurethane types, epoxy ring-opening addition polymer types, poly(meth)acrylic acid types, poly(meth)acrylamide types, polyester types, polyamide types, polyamine types, polyvinyl types and polysaccharide types and complex types of these types.

**[0046]** Polymers in which the side chains of the segment has a repetition of any one or combinations of a hydroxyl group, a carboxyl group or its alkali metal salt, an amino group or its hydrogen halide, a sulfonic acid group or its amine, an alkali metal salt, an alkali earth metal salt and an amide group, and polymers having plural polyoxyethylene groups on a part of these hydrophilic functional groups and principal chain segment are preferable because of their high hydrophilicity. In addition to the above polymers, hydrophilic binder polymers having a urethane bond or a urea bond on the principal chain or the side chain improve not only hydrophilicity but also the printing durability of the non-image portion and are therefore more preferable.

**[0047]** The binder polymer may include as needed various other components described later. Specific examples of the three-dimensionally crosslinked hydrophilic binder polymer are given below. As the hydrophilic binder polymer, at least one of hydrophilic monomers, having a hydroxyl group, carboxylic group or its salt, sulfonic acid group or its salt, phosphoric acid group or its salt, amide group, amino group and ether group, such as (meth)acrylic acid or its alkali or amine salt, itaconic acid or its alkali or amine salt, 2-hydroxyethyl(meth)acrylate, (meth)acrylamide, N-monomethylol(meth)acrylamide, N-dimethylol(meth)acrylamide, 3-vinylpropionic acid or its alkali or amine salt, vinylsulfonic acid or its alkali or amine salt, 2-sulfoethyl(meth)acrylate, polyoxyethylene glycol mono(meth)acrylate, 2-acrylamide-2-methylpropanesulfonic acid, acid phosphoxypolyoxyethylene glycol mono(meth)acrylate and allylamine or mineral acid salt thereof is used to synthesize a hydrophilic homo- or co-polymer.

**[0048]** The hydrophilic binder polymer, having functional groups such as a hydroxyl group, a carboxyl group, an amino group or its salt, or an epoxy group in the hydrophilic polymer, uses these functional groups to obtain an unsaturated group-containing polymer into which an additional polymerization double bond, such as a vinyl group, an allyl group, or a (meth)acryl group, or a ring-forming group, such as a cinnamoyl group, a cinnamylidene group, a cyanocinnamylidene group or a p-phenylenediacylate, has been introduced. As needed, a monofunctional or polyfunctional monomer copolymerizable with the unsaturated group, an initiator (described later), and other components may be added to the polymer and dissolved in an appropriate solvent to prepare a dope. The aforementioned support is coated with the dope, which is then three-dimensionally crosslinked either after or while being dried.

**[0049]** The hydrophilic binder polymer having active hydrogen such as a hydroxyl group, an amino group or a carboxyl group is added to the aforementioned active hydrogen-excluding solvent together with an isocyanate compound or a block polyisocyanate compound and other components described later. The dope is mixed, applied to the support, and reacted either after or while being dried to effect three-dimensional crosslinking. A monomer having a glycidyl group such as glycidyl(meth)acrylate or a carboxylic group such as (meth)acrylic acid may be used in combination with the copolymer components of the hydrophilic binder polymer. The hydrophilic binder polymer having a glycidyl group may be crosslinked three-dimensionally by using, as a crosslinking agent, an  $\alpha,\omega$ -alkane- or alkene-dicarboxylic acid such as 1,2-ethanedicarboxylic acid or adipic acid, polycarboxylic acid such as 1,2,3-propanetricarboxylic acid or trimellitic acid, polyamine compound such as 1,2-ethanediamine, diethylenediamine, diethylenetriamine or  $\alpha,\omega$ -bis-(3-aminopropyl)-polyethylene glycol ether, oligoalkylene or polyalkylene glycol such as ethylene glycol, propylene glycol, diethylene glycol or tetraethylene glycol or polyhydroxy compound such as trimethylolpropane, glycerol, pentaerythritol or sorbitol and by utilizing a ring-opening reaction with each of these compounds.

**[0050]** The hydrophilic binder polymer having a carboxylic group or an amino group may be crosslinked three-dimensionally by utilizing an epoxy ring-opening reaction or the like using, as a crosslinking agent, a polyepoxy compound such as ethylene or propylene glycol diglycidyl ether, polyethylene or polypropylene glycol diglycidyl ether, neopentyl glycol diglycidyl ether, 1,6-hexane diol diglycidyl ether or trimethylolpropane triglycidyl ether.

**[0051]** The hydrophilic binder polymer formed of a polysaccharide such as a cellulose derivative, or the hydrophilic binder polymer in which polyvinyl alcohol or its partially saponified product, glycidol homo- or co-polymer have been taken as its base can be made to possess a three-dimensional structure by introducing the aforementioned crosslinkable functional group by utilizing a hydroxyl group contained in these compounds using the aforementioned method.

**[0052]** Preferable examples of the aforementioned three-dimensionally crosslinked hydrophilic polymers include those obtained by three-dimensionally crosslinking a hydrophilic homo- or co-polymer synthesized using at least one type selected from hydrophilic monomers, such as a (meth)acrylic acid or its alkali metal or amine salt, itaconic acid or its alkali metal or amine salt, 2-hydroxyethyl(meth)acrylate, (meth)acrylamide, N-monomethylol(meth)acrylamide, N-dimethylol(meth)acrylamide, allylamine or its hydroacid halide, 3-vinylpropionic acid or its alkali metal or amine salt, vinylsulfonic acid or its alkali metal or amine salt, 2-sulfoethylene(meth)acrylate, polyoxyethylene glycol mono(meth)acrylate, 2-acrylamide-2-methylpropanesulfonic acid, acid phosphoxypolyoxyethylene glycol mono(meth)acrylate or allylamine or its hydroacid halide, having a hydrophilic group such as a carboxylic group, sulfonic acid group, phosphoric acid and amino group or salts of these groups, hydroxyl group, amide group or ether group or by three-dimensionally crosslinking a hydrophilic binder polymer constituted of a polyoxymethylene glycol or a polyoxyethylene glycol by using the aforementioned method.

**[0053]** The three-dimensionally crosslinked hydrophilic polymers described above are important materials as a matrix for the heat-insulating intermediate layer. However, in order to be made hydrophilic by the alkali developing processing, it is essential that the heat-insulating material according to the present invention has a compound, particularly a polymer organic or inorganic compound, having a hydroxyl group, a primary amino group, a secondary amino group, an acid group (particularly, a phenol group, an imide group, a sulfonamide group, a mercapto group, a carboxylic acid group, a sulfonic acid group, a phosphoric acid group, a phosphonic acid group and a silicic acid group) or an acid group precursor (particularly, alkylesters, arylestere, acid anhydrides or acid halides), which are functional groups that become hydrophilic or whose hydrophilicity is strengthened when the groups react with an alkali or a silicate in a developing solution.

**[0054]** However, these techniques are so-called cross-linkable hydrophilic layers that were developed simply as a means to impart hydrophilicity to a hydrophobic support. When such hydrophilic layers are used as they are for the heat-insulating material of the present invention, the hydrophilicity becomes too high and sometimes adhesion with the adjacent photosensitive layer is made worse. For this reason, the above hydrophilic layer technique is combined with two techniques described below in order to form a heat-insulating layer that can be made hydrophilic and can be appropriately used in the present invention.

**[0055]** A first technique is that in which an adhesive is combined with the cross-linkable hydrophilic layer. A second technique is that in which a processing for improving adhesion by regulating hydrophilicity/hydrophobicity is administered, but details of this second technique will be described later.

**[0056]** First, the first technique in which an adhesive is combined with the cross-linkable hydrophilic layer will be described.

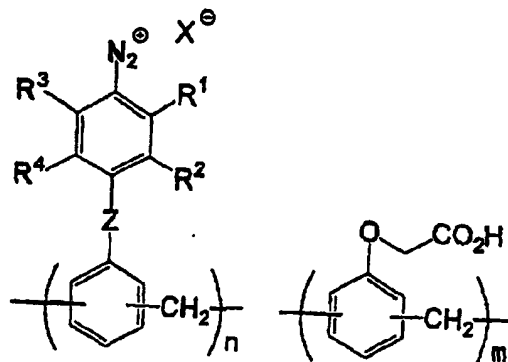
**[0057]** One example concerns a technique in which an adhesive (described later) for improving adhesion with the photosensitive layer is incorporated in the material of the hydrophilic layer, thereby imparting to the heat-insulating intermediate layer itself a high adhesion with the infrared-sensitive layer (i.e., the recording layer). Another example concerns a technique in which an adhesive layer having an adhesive is disposed between the heat-insulating intermediate layer and the recording layer to thereby ensure the adhesion of both.

**[0058]** Examples of such an adhesive include one or more types selected from phosphonic acids having an amino group such as carboxymethyl cellulose, dextrin, gum arabic and 2-aminoethylphosphonic acid; organic phosphonic acid such as phenylphosphonic acid, naphthylphosphonic acid, alkylphosphonic acid, glycerophosphonic acid, methylenediphosphonic acid and ethylenediphosphonic acid which may have a substituent; organic phosphoric acid such as phenylphosphoric acid, naphthylphosphoric acid, alkylphosphoric acid and glycerophosphoric acid which may have a substituent; organic phosphinic acid such as phenylphosphinic acid, naphthylphosphinic acid, alkylphosphinic acid and glycerophosphinic acid which may have a substituent; amino acids such as glycine and  $\beta$ -alanine; and hydrochloride of amines having a hydroxyl group such as hydrochlorides of triethanolamine. These may be used by mixing two or more.

**[0059]** Compounds represented by the following general formulae ZZ-1 to ZZ-6 are particularly preferable as adhesives:

**[0060]** A diazonium polymer (weight average molecular weight 1,000 to 20,000) is represented by the following general formula ZZ-1:

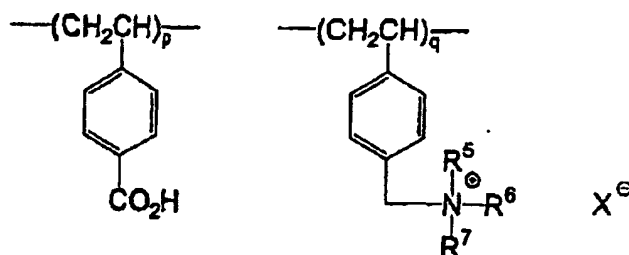
ZZ-1)



**[0061]** In the formula,  $R^1$  to  $R^4$  independently represent a hydrogen atom, an alkyl group with a carbon number of 1 to 12, and an alkoxy group having an alkyl group with a carbon number of 1 to 12, Z represents O, S or NH, and  $X^-$  represents a counter-anion selected from  $Cl^-$ ,  $Br^-$ ,  $PF_6^-$ ,  $BF_4^-$ ,  $ClO_4^-$ , arylsulfonic acid anion and alkylsulfonic acid anion, and  $n \neq 0$  but m may be zero.

**[0062]** A copolymer (weight average molecular weight 1,000 to 50,000) of vinylbenzoic acid is represented by the general formula ZZ-2,

ZZ-2)



**[0063]** In the formula,  $R^5$  to  $R^7$  independently represent an alkyl group with a carbon number of 1 to 12, an aryl group, and an aralkyl group,  $X^-$  represents a counter-anion as in the formula ZZ-1, and  $p \neq 0$  but q may be zero.

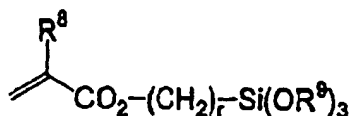
**[0064]** When the molecular weight of any of the aforementioned copolymer is less than the range described above, the effect of adhesion is diminished. When the molecular weight of the same is greater than the range described above, there is the risk that it cannot be taken off at the time of developing and that printing contamination will arise. Therefore, it is preferable to use a copolymer having a molecular weight that falls within the range prescribed above.

**[0065]** The compounds of the remaining general formulae are a polymerizable silane coupling agent represented by the general formula ZZ-3, a polymer compound (weight average molecular weight 1000 to 50,000) having a silane coupling moiety represented by the general formula ZZ-4, polymerizable phosphonic acid or polymerizable phosphoric acid represented by the general formula ZZ-5, and a polymer compound (weight average molecular weight 1,000 to 50,000) represented by the general formula ZZ-6 having two or more adjoining hydroxyl groups on the benzene ring.

**[0066]** It is particularly effective to use these compounds as an adhesive layer by coating by a sol-gel processing with tetra-alkoxysilane in the presence of an acid catalyst (phosphoric acid, sulfuric acid, hydrochloric acid or organic sulfonic acid) or a basic catalyst (ammonia, KOH or NaOH). In particular, the compounds are appropriately used as a recording layer when a radical polymerizable recording layer is used.



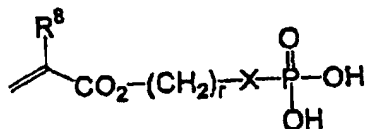
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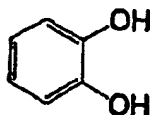
ZZ-4)



ZZ-5)



ZZ-6)



[0067] In the formula,  $\text{R}^8$  denotes a methyl group,  $\text{R}^9$  denotes a methyl, ethyl or phenyl group, and  $r$  and  $n$  represent integers of 2 to 20 and 1 to 3, respectively.  $X$  represents O or a single bond.

[0068] When a polymer having a hydroxyl group at the side chains thereto is used as the hydrophilic layer, boric acid, aluminic acid or aluminosilicic acid, or sodium, potassium, ammonium, tetraalkylammonium or organic amine salts of these acids are highly effective for advancing film hardening and for adhesion.

[0069] When these adhesive agents are incorporated in the hydrophilic material, the amount incorporated therein is 0.01wt.% to 50wt.% with respect to the total solid component. When the incorporated amount is less than 0.01wt.%, the effect of adhesion does not emerge. When the incorporated amount is less greater than 50wt.%, it becomes difficult for the effect of the hydrophilic layer to be made manifest.

[0070] When these adhesive agents are formed on the surface of the hydrophilic layer as an adhesive layer (an organic undercoat layer), an appropriate amount of coating is 1 to 500  $\text{mg}/\text{m}^2$ , more preferably 1 to 100  $\text{mg}/\text{m}^2$ , and most preferably 1 to 50  $\text{mg}/\text{m}^2$ . When the amount of coating is less than 1  $\text{mg}/\text{m}^2$ , the effect of improving the adhesion becomes insufficient. When the coating amount is greater than 500  $\text{mg}/\text{m}^2$ , there is a tendency for the hydrophilization processing resulting from permeation of the developer to be obstructed, such that the layer cannot be made hydrophilic and printing contamination is generated.

[0071] The organic undercoat layer may be disposed by a method such as the following methods. In one method, a solution prepared by dissolving the foregoing organic compound in water, or in an organic solvent such as methanol, ethanol and methylethyl ketone, or in a mixed solvent thereof, is coated on a support having a heat-insulating intermediate layer or on a heat-insulating support comprising a hydrophilic layer, then dried. In another method, a solution prepared is by dissolving the foregoing organic compound in water, or in an organic solvent such as methanol, ethanol and methylethyl ketone, or in a mixed solvent thereof, and then the support is immersed in the solution so that the support is made to adsorb the aforementioned compound. Thereafter, the support is washed with water or the like and dried to provide the organic undercoat layer. In the former method, a solution having a concentration of 0.05wt.% to 10wt.% of the organic compound may be coated by a variety of methods. In the latter method, the concentration of the solution is 0.01 to 20% by weight, preferably 0.05 to 5% by weight, the dipping temperature is 20 to 90°C, preferably

25 to 50°C, and the dipping time is 0.1 second to 20 minutes, preferably 2 seconds to 1 minute. The pH of the solution to be used may be adjusted from 1 to 12 using a basic substance such as ammonia, triethylamine or potassium hydroxide, or an acidic substance such as hydrochloric acid or phosphoric acid. When the recording layer of the present invention is used as a printing plate for lithography, a yellow dye may be added in order to enhance tonal reproducibility.

**[0072]** The second technique for improving adhesion will be described hereinafter. In this technique, adhesion is improved by the adjusting the hydrophilic-hydrophobic balance of the heat-insulating material.

**[0073]** Specifically, the second technique is a method in which the number of hydrophilic groups in the components included in the hydrophilic layer suitable as a heat-insulating material is decreased or the number of hydrophobic groups in the same is increased, whereby the hydrophilicity/hydrophobicity balance is adjusted, a certain degree of hydrophobicity is imparted to the surface and adhesion is improved. As mentioned previously, when the number of hydrophilic groups is large and the hydrophilicity is too high, adhesion with the adjacent infrared-sensitive layer drops. Here, however, the possibility emerges that contamination may be generated in the non-image portions when measures to reduce the functional groups, which function to make hydrophilicity manifest in the heat-insulating intermediate layer or the heat-insulating support surface by making contact with the alkali developing solution, or measures to suppress the function of the functional groups are taken. Accordingly, it is preferable to adjust the hydrophilicity/hydrophobicity balance without exerting a large influence on the functional groups having such a function. Examples of means for doing so include increasing the prepared amount of compounds having hydrophobic groups at the time the matrix of the heat-insulating material is formed, or adjusting the number of functional groups by lowering the amount of compounds introduced when there are compounds having hydrophilic functional groups that are not used in the reaction with the alkali developing solution.

**[0074]** Whether or not the heat-insulating layer (i.e., the heat-insulating intermediate layer or the heat-insulating support of the present invention), which can be made hydrophilic and has been obtained by administering an adhesion-improving processing to the cross-linkable hydrophilic material in accordance with the preceding techniques, is suitable for the object of the present invention can be judged by measuring the surface contact angle of water drops in the air. Adhesion with the recording layer may be judged to be good when the contact angle of water drops in the air is within a range of 10° to 100°, preferably 30° to 100°, and more preferably 50° to 100°. When the value is lower than 10°, adhesion with the photosensitive layer becomes weak, and peeling of the surface due to permeation of the developing solution at the time of developing easily occurs. When the value is greater than 100°, the developing is completely repelled and permeation of the developing solution is suppressed, thus making it difficult to administer hydrophilicization processing.

**[0075]** Hereinafter, the infrared-sensitive layer (negative-type radical polymerization recording layer), whose alkali developability is changed by the action of an infrared ray and which the heat-sensitive planographic plate of the present invention has on the heat-insulating material, will be described. The infrared-sensitive layer that is used here is a layer whose solubility in an alkali developing solution is changed by the irradiation of an infrared laser. It is necessary that substantially no ablation occurs at the time the solubility is changed. Namely, in the present invention, a change in the solubility of the recording layer refers to a change in solubility only with respect to the alkali developing solution, unattended by other phenomena, and is not meant to include elimination resulting from scattering of the recording layer.

**[0076]** The recording layer can be divided into two types: a negative-type in which alkali developability is lowered by the action of an infrared light, and a negative-type layer in which alkali developability is raised by the action of an infrared light.

**[0077]** The negative-type recording layer is radical polymerization based, which is preferable among the recording layers from the aspect of tolerance to repeated printings. Radicals generated by light irradiation or heating serve as an initiator or a catalyst, and the compounds structuring the recording layer trigger a polymerization reaction and a cross-linking reaction and harden to form image portions.

**[0078]** The present invention provides a heat-insulating support or a heat-insulating intermediate layer capable of being made hydrophilic at the time of developing processing, through which effect sensitivity is raised and printing performance is improved. The present invention is not affected by the materials structuring the recording layer.

#### Radical Polymerization Layer

**[0079]** The radical polymerization layer used as the recording material of the planographic printing plate of the present invention has a compound that generates radicals by light or heat (referred to as a radical generator hereinafter), and a compound polymerizable by radicals (referred to as a polymerizable compound hereinafter). For example, radicals are generated at exposed portions from the radical generator by the irradiation of an infrared laser or the like, the radicals become initiators and the polymerizable compound is hardened by a radical polymerization reaction, whereby image portions are formed. The combination of the radical generator and polymerizable compound used here may be appropriately selected from known combinations, provided that the strength of the film formed by the radical polymerization satisfies demands as a recording layer. Accelerators such as onium salts and infrared absorbers may be used

together for improving reactivity of the radical generator. Examples of components that can be used for the radical polymerization layer include, for example, the compound disclosed in Japanese Patent Application Laid-Open (JP-A) No. 8-108621 as a structural component of a heat-polymerizable recording layer, and the compound disclosed in JP-A No. 9-34110 as a structural component of a photosensitive layer.

#### Radical Generator

**[0080]** Known radical polymerization initiators generally used in polymer synthesis reactions caused by radical polymerization may be used without restriction as the radical generator to be used for the radical polymerization layer. Examples include azobisnitrile compounds such as 2,2'-azobisisobutyronitrile and 2,2'-azobispropionitrile; peroxides such as benzoyl peroxide, lauroyl peroxide, acetyl peroxide, t-butyl perbenzoate,  $\alpha$ -cumyl hydroperoxide, di-t-butyl peroxide, diisopropyl peroxydicarbonate and t-butyl peroxyisopropyl carbonate; alkyl peroxy carbamates; organic peroxides such as nitrosoaryl acylamine; inorganic peroxides such as potassium persulfate, ammonium persulfate and potassium perchlorate; diazo compounds such as diazoaminobenzene, p-nitrobenzene diazonium, azobis-substituted alkanes, diazothioethers and arylazosulfones; tetraalkyl tiuramdisulfides such as nitrosophenyl urea and tetramethylthiuram disulfide; diaryl disulfides such as dibenzoyl disulfide; dialkyl xantic acid disulfides; aryl sulfines; aryl alkylsulfones; and 1-alkane sulfines.

**[0081]** Although it depends on the energy of the laser, sufficient sensitivity can be obtained even with a radical generator having a large activation energy, because the temperature of the exposed surface can reach up to 600°C when the planographic printing plate of the present invention is recorded with an infrared laser.

**[0082]** The activation energy of the radical generator for generating radicals is preferably 30 Kcal/mole or more, and examples of such radical generators include azobisnitrile compounds and organic peroxides. Compounds whose stability at room temperature is excellent, whose speed of decomposition when heated is rapid, and which become colorless at the time of decomposition are preferable. Examples of such compounds include benzoyl peroxide, 2,2'-azobisisobutyronitrile and the like.

**[0083]** The radical generators described above may be used singly, or in combination of two or more, and are used in an amount of 0.5 to 30% by weight, preferably 2 to 20% by weight, relative to the total solid component of the radical polymerization layer.

**[0084]** Compounds that generate radicals by interacting with onium salt (described later) may also be appropriately used. Specifically, examples of such compounds include halides ( $\alpha$ -haloacetophenones, trichloromethyl triazines and the like), azo compounds, aromatic carbonyl compounds (benzoyl esters, ketals, acetophenones, o-acyloxyimino ketones, acylphosphine oxides and the like), hexaaryl bismidazole compounds and peroxides. Preferably, the bisimidazole derivative disclosed as A-1 to A-4 on p. 16 of Japanese Patent Application Laid-Open (JP-A) No. 9-24110 may be used.

**[0085]** The latter radical generator can attain high sensitivity by interacting with an onium salt. Examples of onium salts that can be used together with the radical generator include such compounds as the phosphonium salts, sulfonium salts, iodonium salts and ammonium salts disclosed in paragraphs [0022] to [0049] of JP-A No. 9-34110.

**[0086]** The amount of the onium salt added is preferably in the range of 0.05 to 50% by weight relative to the total solid component of the recording layer, although the amount differs depending on the kind and the mode of use of the onium salt.

#### Polymerizable Compound

**[0087]** Known monomers having a polymerizing group may be used without particular restriction as the polymerizable polymer compound which is polymerized and hardened by radicals generated from the radical generator. Examples of such monomers include monofunctional acrylic acid esters and their derivatives such as 2-ethylhexyl acrylate, 2-hydroxyethyl acrylate and 2-hydroxypropyl acrylate, or compounds in which acrylate was replaced with methacrylate, itaconate, crotonate or emalate; bifunctional acrylic esters and their derivatives such as polyethyleneglycol diacrylate, pentaerythritol diacrylate, bisphenol A diacrylate and diacrylate of hydroxyphenyl acid neopentyl alcohol  $\epsilon$ -caprolactone adduct, and or compounds in which these acrylates are replaced with methacrylate, itaconate, crotonate and emalate; and multifunctional acrylic acid esters and their derivatives such as trimethylolpropane (metha)acrylate, dipentaerythritol pentaacrylate, dipentaerythritol hexaacrylate and pyrogallol triacrylate, or compounds in which these acrylates are replaced with methacrylate, itaconate, crotonate and emalate. So-called pre-polymers, prepared by introducing acrylic acid or methacrylic acid into an oligomer having an appropriate molecular weight to impart a photopolymerizing property, may be favorably used.

**[0088]** Other examples include such compounds as disclosed in Japanese Patent Application Laid-Open (JP-A) Nos. 58-212994, 61-6649, 62-46688, 62-48589, 62-173295, 62-187092, 63-67189 and 1-244891. The compounds described in "11290 Chemicals", Kagaku Kogyo Nippo Co., pp. 286-194, and in "Handbook of UV/EB Hardening Agents

(Materials) \* Kobunshi Kanko-kai, pp. 11-65 may also be favorably used.

**[0089]** Among these, the compounds having two or more acrylic groups or methacrylic groups in the molecules thereof are preferable in the present invention. The compounds preferably have a molecular weight of 10,000 or less, and more preferably 5,000 or less. In the present invention, in accordance with the object, one type of polymer compound (and if no problems arise in compatibility and affinity, combinations of two or more types of polymer compounds) may be used from the prepolymers and monomers having a polymerizing group, including those monomers given as examples above.

**[0090]** The compounds having ethylenic unsaturated groups are preferably incorporated in the radical polymerization layer as a solid component in a preferable amount of 20 to 80% by weight, and more preferably in an amount of 30 to 60% by weight.

#### Binder Resins

**[0091]** Binder resins may be used in the photosensitive layer as needed. Examples of such binder resins include polyester resins, polyvinyl acetal resins, polyurethane resins, polyamide resins, cellulose resins, olefin resins, vinyl chloride resins, (meth)acrylic resins, styrene resins, polycarbonate, polyvinyl alcohol, polyvinyl pyrrolidone, polysulfone, polycaprolactone resins, polyacrylonitrile resins, urea resins, epoxy resins, phenoxxy resins, and rubber based resins. Resins having unsaturated bonds in the resin, for example diarylphthalate resins and their derivatives, and chlorinated polypropylene, may be favorably used depending on the purpose, since they can be polymerized with the compounds having ethylenic unsaturated bonds described above. One type of binder resin or a combination of two or more among the resins described above may be used for the binder resin.

**[0092]** These binder resins are preferably used in a range of 500 parts by weight or less, and more preferably 200 parts by weight or less, relative to 100 parts by weight of the polymerizable compound.

#### Infrared Absorber

**[0093]** It is preferable in the present invention that the radical polymerization layer includes an infrared absorber that efficiently converts infrared laser light into heat, in order to improve the sensitivity of the radical generator and accelerate the radical polymerization reaction. The infrared absorber to be used herein may be dyes or pigments that effectively absorb infrared light having a wavelength of 760nm to 1200nm. Preferably, the dye or pigment has a absorption maximum at a wavelength of 760nm to 1200nm.

**[0094]** Commercially available and known dyes, such as those described in *Senryō Biran* ("Handbook of Dyes", edited by the Association of Synthetic Organic Chemistry Japan, 1970), may be used. Examples of the dyes and pigments include azo dyes, metal complex azo dyes, pyrazolone dyes, naphthoquinone dyes, anthraquinone dyes, phthalocyanine dyes, carbonium dyes, quinimine dyes, methine dyes, cyanine dyes, squalilium pigments, pyrylium salts and metal thiolate complexes.

**[0095]** Preferable dyes include the cyanine dyes disclosed in Japanese Patent Application Laid-Open (JP-A) Nos. 58-125246, 59-84356, 59-202829 and 60-78787; the methine dyes disclosed in Japanese Patent Application Laid-Open (JP-A) Nos. 58-173696, 58-181690 and 58-194595; the naphthoquinone dyes disclosed in Japanese Patent Application Laid-Open (JP-A) Nos. 58-112793, 58-224793, 59-48187, 59-73996, 60-52940 and 60-63744; the squalilium pigments disclosed in Japanese Patent Application Laid-Open (JP-A) No. 58-112792; and the cyanine dyes described in British Patent No. 434,875.

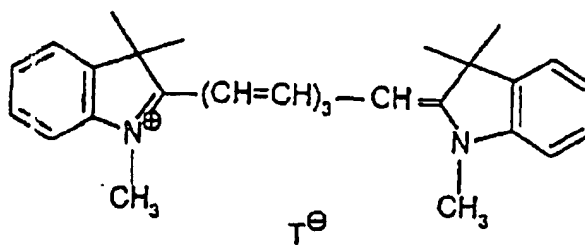
**[0096]** Further, the near infrared absorption intensifier disclosed in USP 5,156,938 may also be suitably used. In addition, the arylbenzo(thio)pyrylium salts disclosed in USP 3,881,924; the trimethylene thiapyrylium salts disclosed in Japanese Patent Application Laid-Open (JP-A) No. 57-142645 (USP 4,327,169); the pyrylium compounds disclosed in Japanese Patent Application Laid-Open (JP-A) Nos. 58-181051, 58-220143, 59-41363, 59-84248, 59-84249, 59-146063 and 59-146061; the cyanine pigments disclosed in Japanese Patent Application Laid-Open (JP-A) No. 59-216146; the pentamethine thiopyrylium salts disclosed in USP 4,283,475; and the pyrylium compounds described in Japanese Patent Application Publication (JP-B) Nos. 5-13514 and 5-19702 may also be preferably used.

**[0097]** Other examples of preferable dyes include the near infrared absorption dyes disclosed in USP 4,756,993 as the formulae (I) and (II).

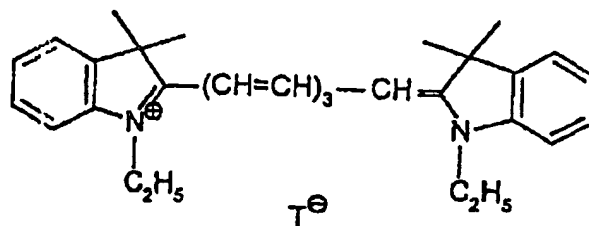
**[0098]** Particularly preferable among these dyes are cyanine pigments, squalirylum pigments, pyrylium salts, and nickel thiolate complexes.

**[0099]** Favorable examples of the infrared absorber to be used in the present invention include those having an onium salt structure as described below. By using such infrared absorbers, the addition of the onium salts described above may be omitted, or the added amount of onium can be reduced. Specific examples of infrared absorbers having an onium salt structure are shown in A-1 to A-56, but the present invention is not restricted thereto.

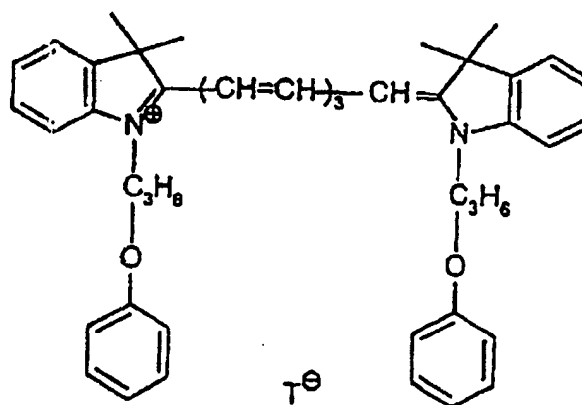
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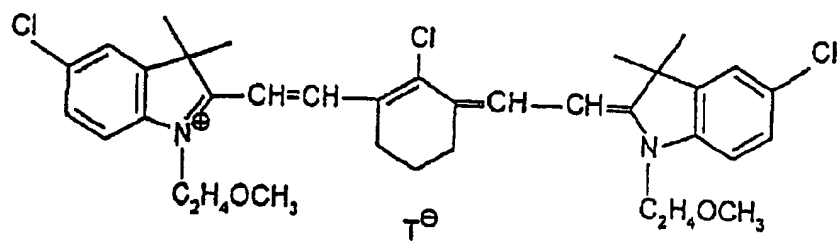
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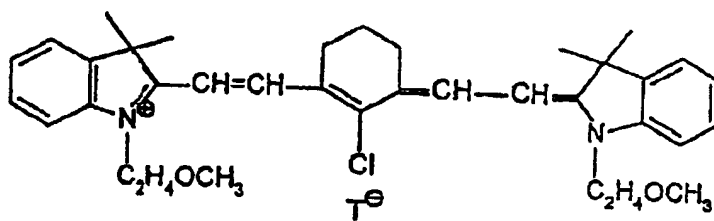
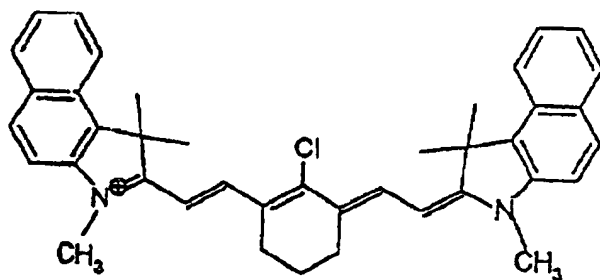
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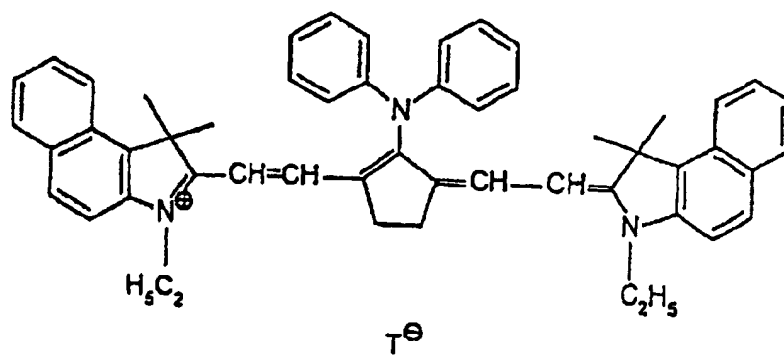
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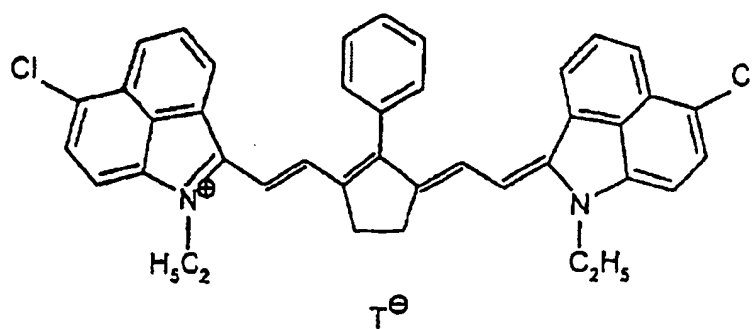
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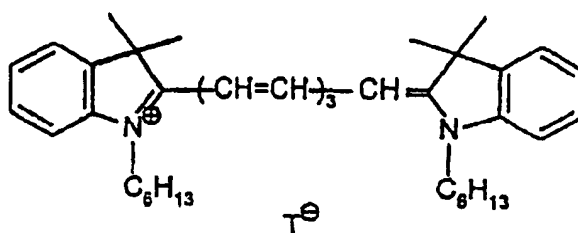
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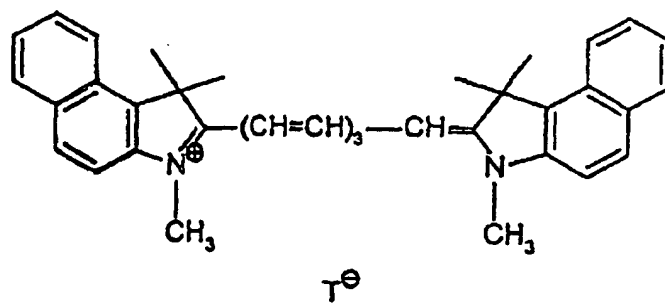
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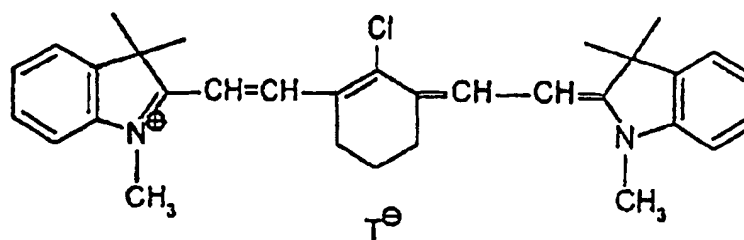
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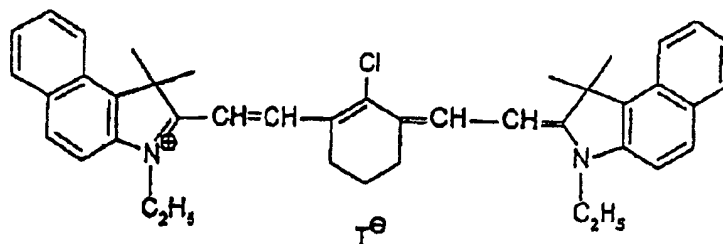


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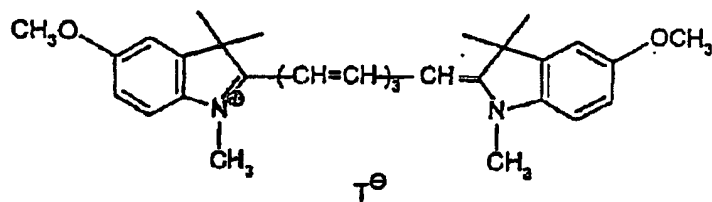


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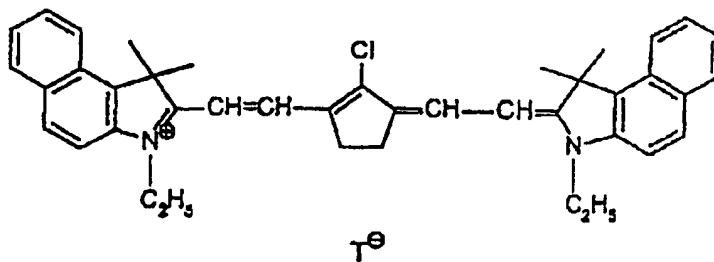
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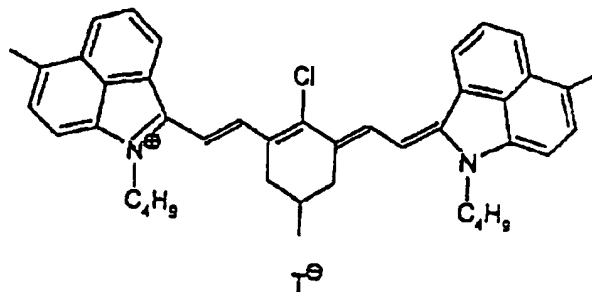


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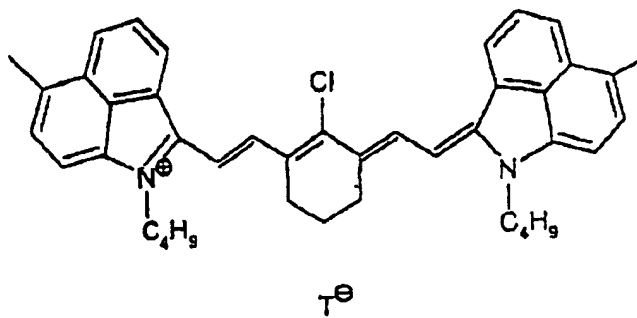
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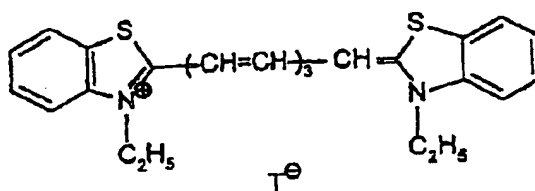




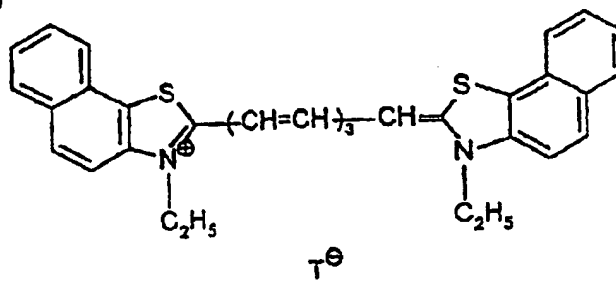
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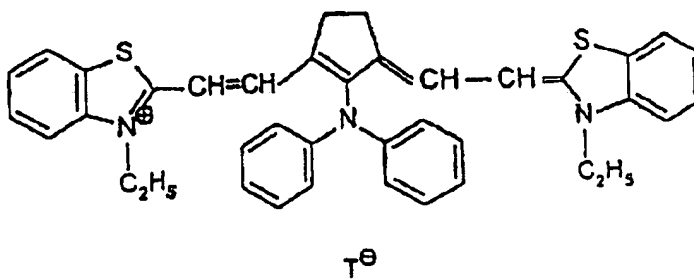
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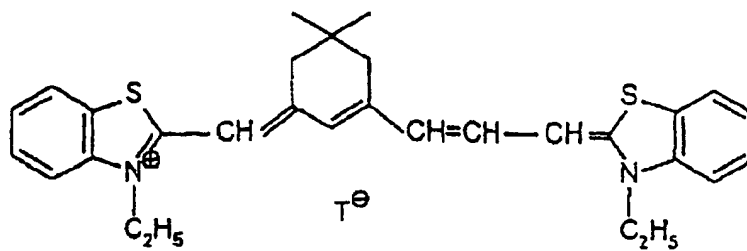
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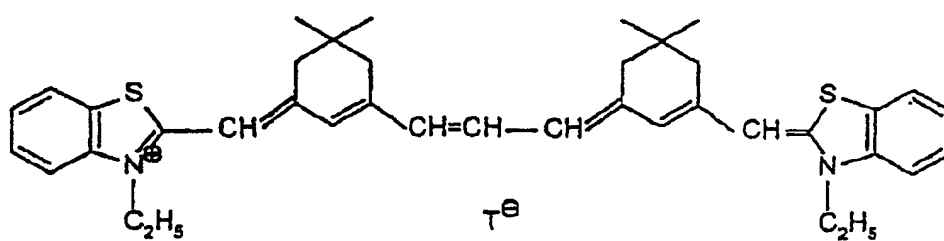


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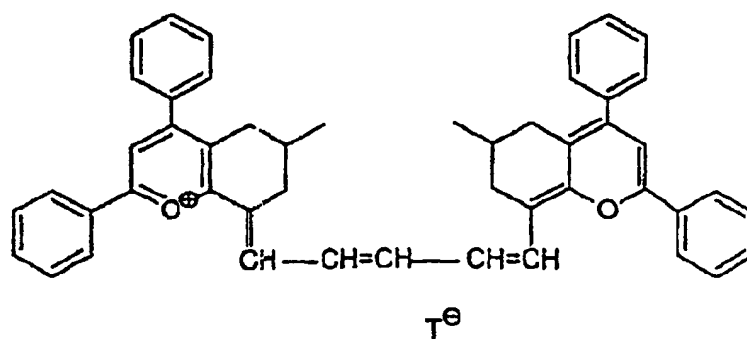


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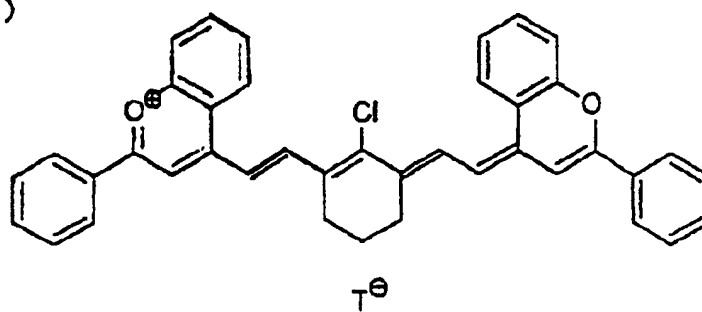


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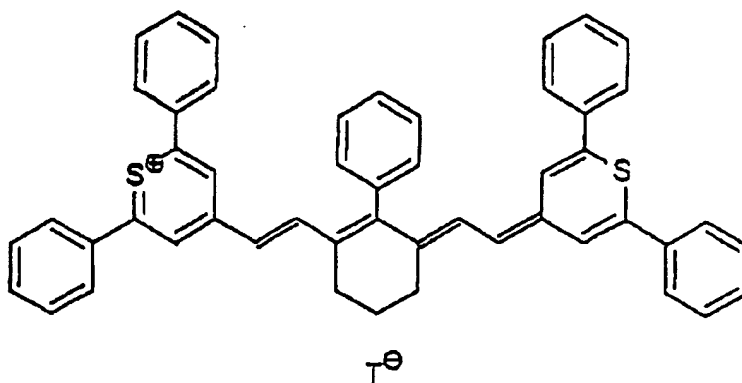
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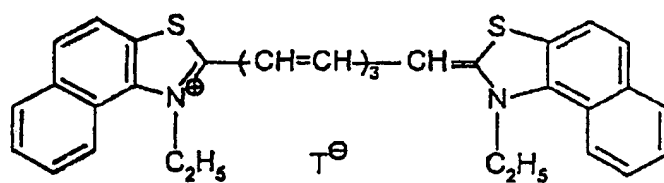
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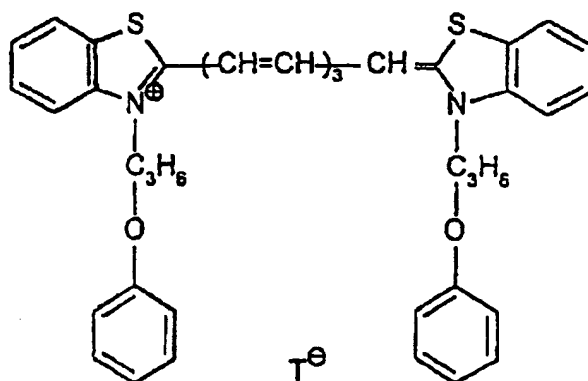
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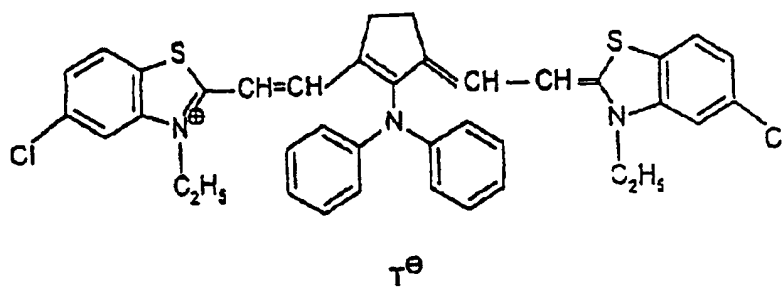
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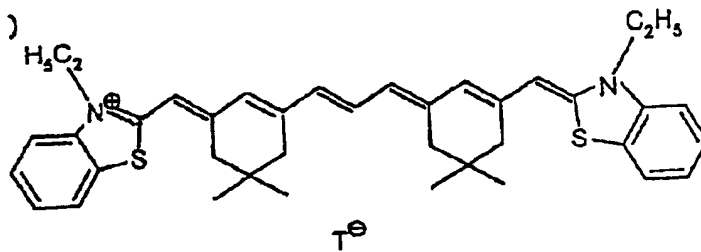
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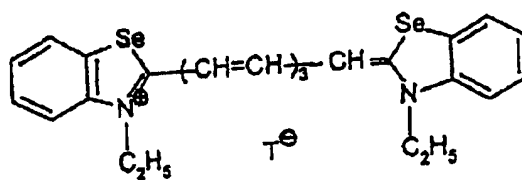
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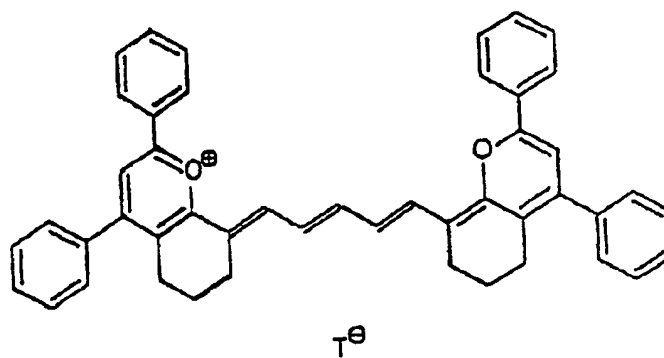
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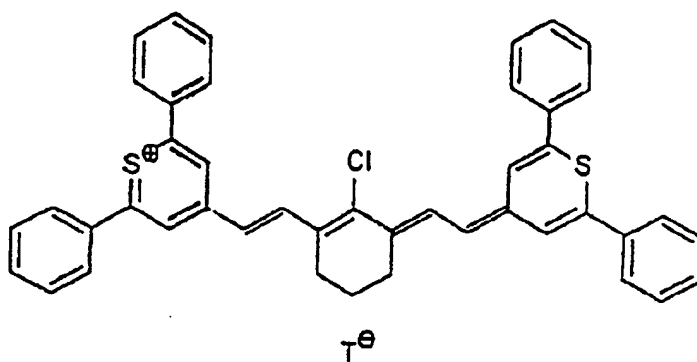
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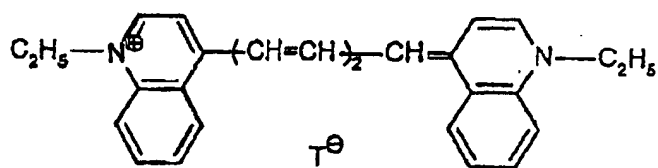
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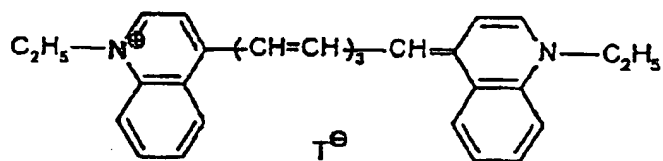
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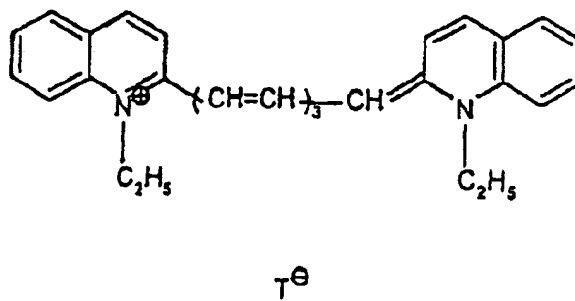
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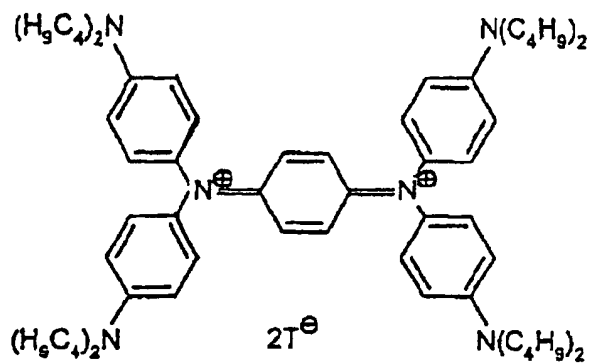
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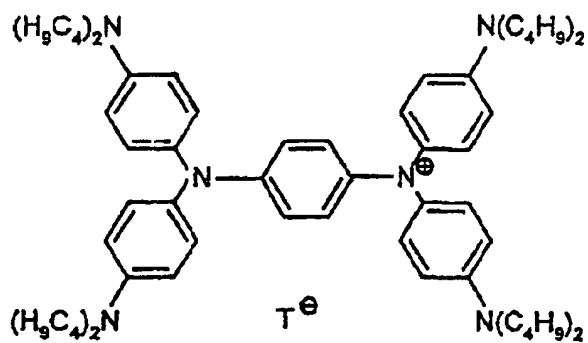
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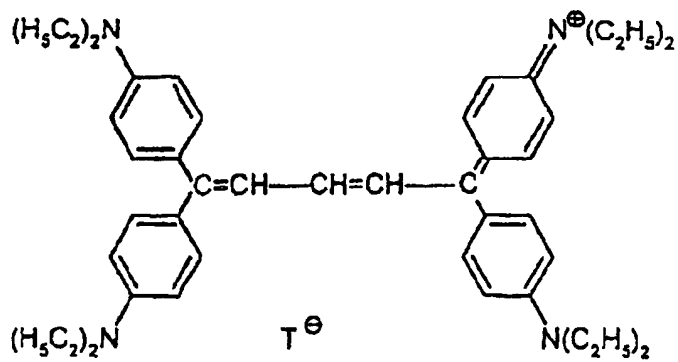
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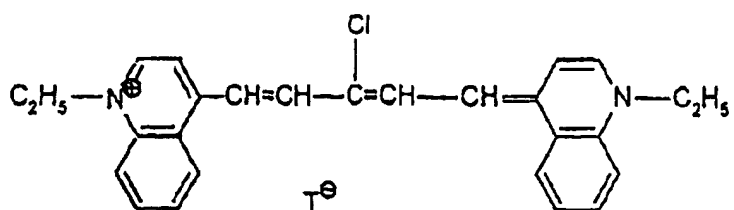
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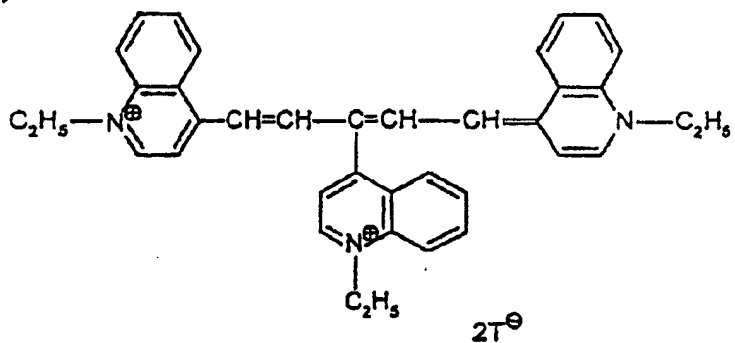
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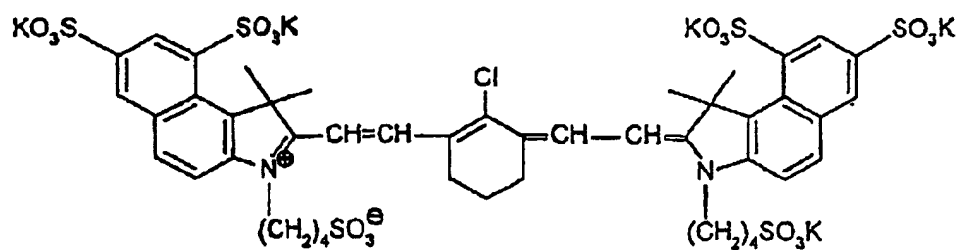
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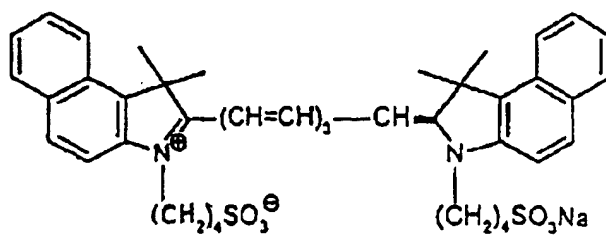
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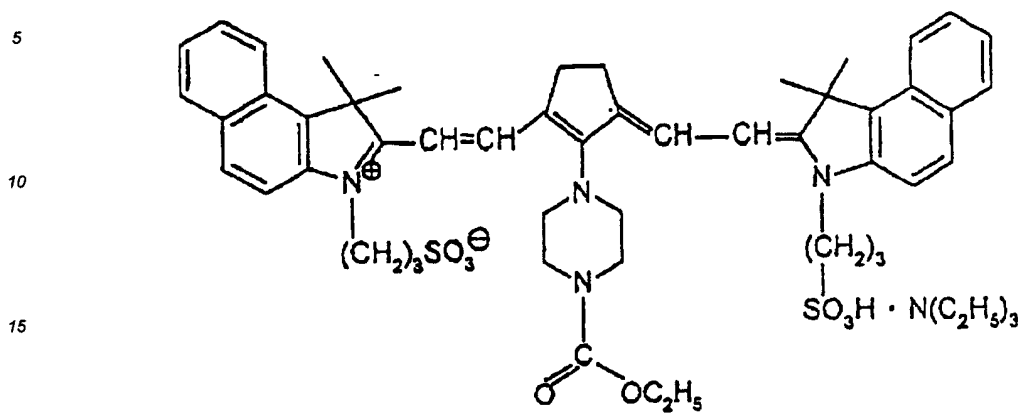
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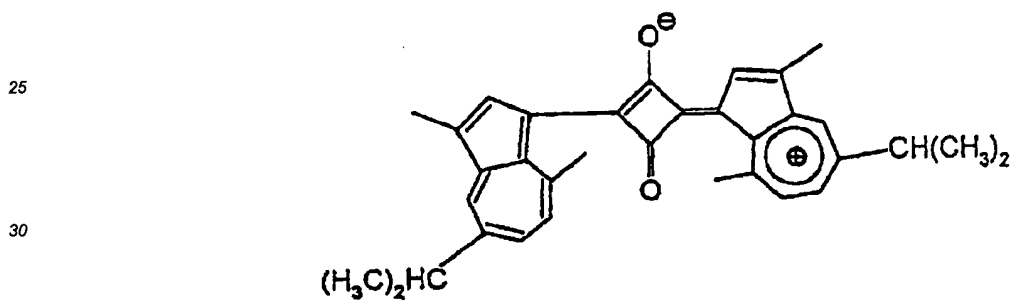
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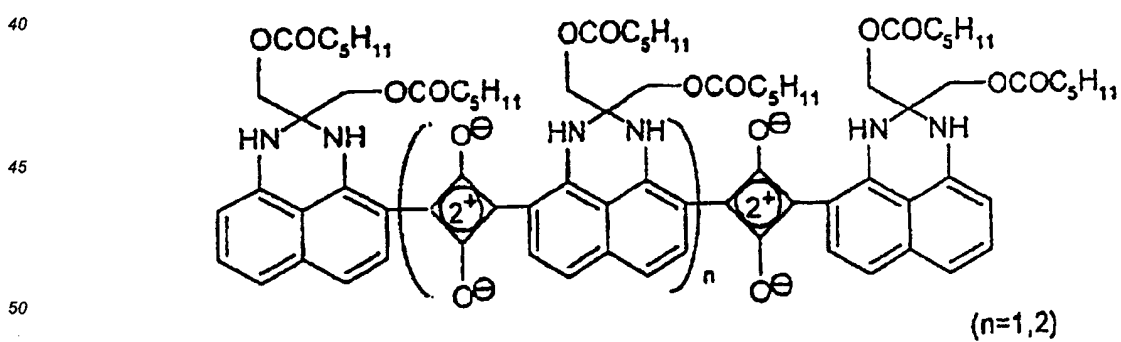
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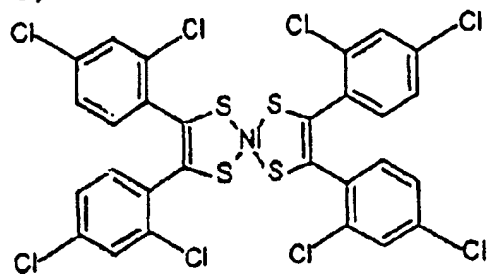


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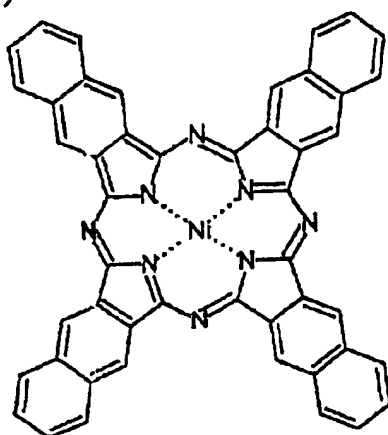




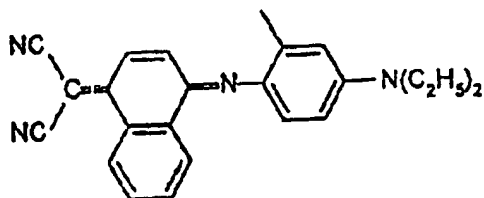
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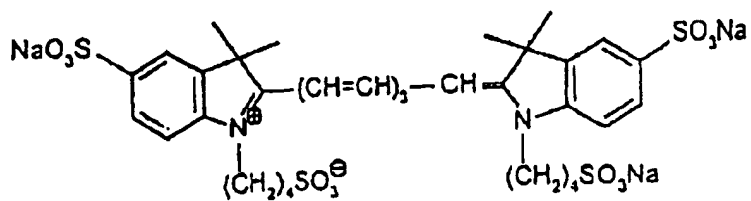
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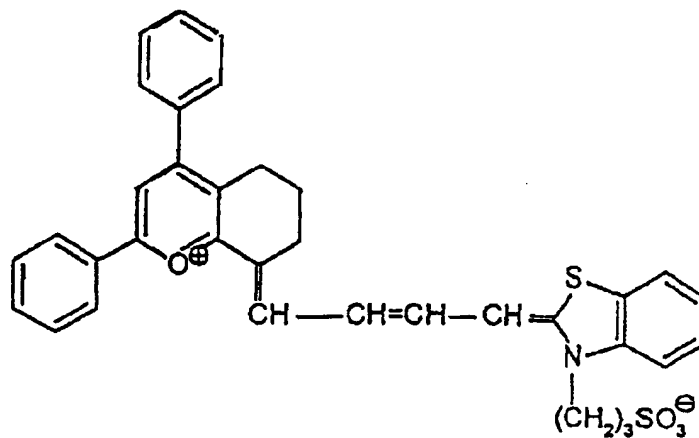
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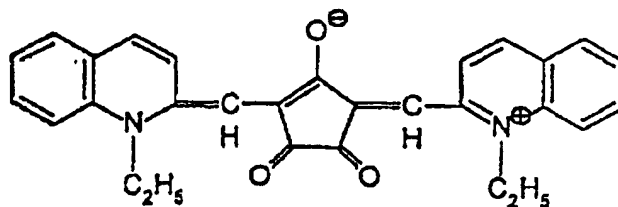
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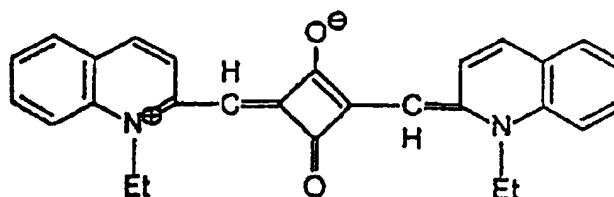
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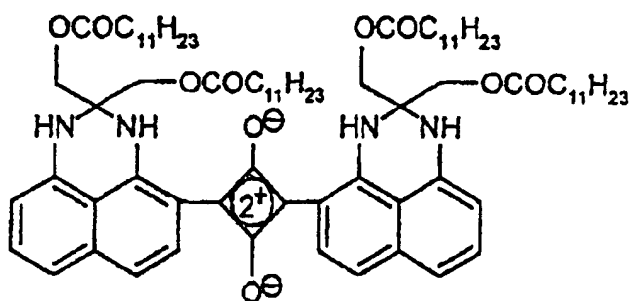
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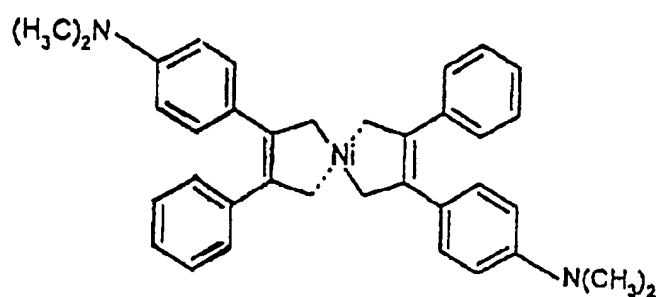
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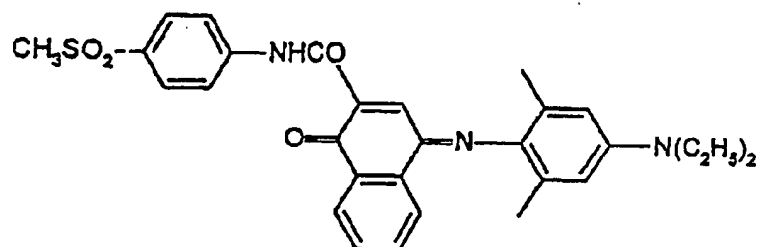
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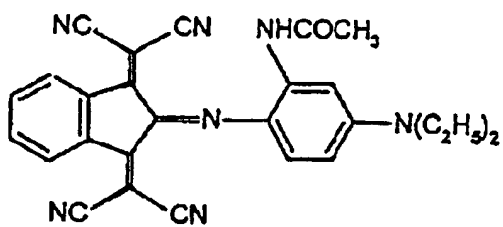
A - 5 3 )



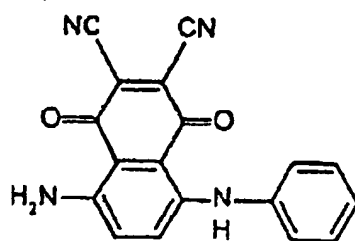
A - 5 4 )



A - 5 5 )



A - 5 6 )



**[0100]** In the structural formulae A-1 to A-56, T<sup>-</sup> denotes a univalent counter anion, preferably a halogen anion (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup> or I<sup>-</sup>), a Lewis acid anion (BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, SbCl<sub>6</sub><sup>-</sup> or ClO<sub>4</sub><sup>-</sup>), an alkylsulfonic acid anion or an arylsulfonic acid anion.

**[0101]** The alkyl group as used here denotes a straight-chain, branched or ring alkyl group with a carbon number of 1 to 20. Specifically, examples include methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, hexadecyl, octadecyl, eicosyl, isopropyl, isobutyl, s-butyl, t-butyl, isopentyl, neopentyl, 1-methylpropyl, isohexyl, 2-ethylhexyl, 2-methylhexyl, cyclohexyl, cyclopentyl or 2-norbonyl groups. Straight-chain alkyl groups with a carbon number of 1 to 12, branched alkyl groups with a carbon number of 3 to 12, and ring alkyl groups with a carbon number of 5 to 10 are preferable among these examples.

**[0102]** The aryl group used here refers to an aryl group of one benzene ring, an aryl group formed of a condensed ring of two or three benzene rings, or an aryl group in which a benzene ring and five-member unsaturated ring form a condensed ring. Specific examples include phenyl, naphthyl, anthoryl, phenanthoryl, indenyl, acenaphthenyl and fluorenyl groups. The phenyl and naphthyl groups are more preferable among them.

**[0103]** Examples of pigments that may be used for the infrared absorber in the present invention include commercially available pigments and pigments described in the *Color Index* (C.I.) catalog, *Saishin Ganryô Binran* ("Recent Pigment Catalog" (edited by the Japan Pigment Technology Association, 1977), *Saishin Ganryô Ôyô Gijutsu* ("Recent Pigment Application Technology", published by CMC, 1986), and *Insatsu Inki Gijutsu* ("Ink Printing Technology", published by CMC, 1984).

**[0104]** Examples of the kinds of the pigments include black pigments, yellow pigments, orange pigments, brown pigments, red pigments, purple pigments, blue pigments, green pigments, fluorescent pigments and metal powder pigments, as well as polymer bound pigments. Specifically, insoluble azo pigments, azo complex pigments, condensation pigments, complex azo pigments, phthalocyanine pigments, anthraquinone pigments, perylene and perynone pigments, thioindigo pigments, quinacridon pigments, dioxadine pigments, isoindolinone pigments, qinophthalocyanine pigments, staining lake pigments, azine pigments, nitroso pigments, nitro pigments, natural pigments, fluorescent pigments, inorganic pigments and carbon black.

**[0105]** These pigments may be used without surface treatment or after a surface treatment has been administered thereto. Examples of surface treatment methods include a method in which the surface is coated with a resin or wax, a method in which a surfactant is adhered, and a method in which a reactive substance (e.g., a silane coupling agent, an epoxy compound, polyisocyanate and the like) is bonded to the pigment surface. These surface treatment methods are described in *Kinzoku Sekken no Seishitsu to Ôyô* ("Properties and Application of Metallic Soap", published by Saiwai Shobô), *Insatsu Inki Gijutsu* ("Ink Printing Technology", published by CMC, 1984), and *Saishin Ganryô Ôyô Gijutsu* ("Recent Pigment Application Technology", published by CMC, 1986).

**[0106]** The particle diameter of the pigment is preferably in the range of 0.01 µm to 10 µm, more preferably in the range of 0.05 µm to 1 µm, and even more preferably in the range of 0.1 µm to 1 µm. A pigment particle diameter of less than 0.01 µm is not preferable from the standpoint of acid cross-linking of dispersed material and stability of the polar conversion layer in the coating solution. A particle diameter of more than 10 µm is also not preferable from the standpoint of uniformity of the recording layer.

**[0107]** Known dispersion methods used in the manufacture of inks and toners may also be used as a method for dispersing the pigment. Examples of dispersing machines include a ultrasonic dispersing machine, a sand mill, an atoliter, a pearl mill, a super mill, a ball mill, an impeller, a dispersor, a KD mill, a colloid mill, a dynatron, a three-axis roll mill and a pressurizing kneader. Details are described in *Saishin Ganryô Ôyô Gijutsu* ("Recent Pigment Application Technology", published by CMC, 1986).

**[0108]** In addition, other compounds, such as the compound disclosed as a "photo-thermal conversion substance" in JP-A No. 8-108621 and the compound disclosed as a "photo-thermal conversion element" in JP-A No. 9-34110, may also be similarly used.

**[0109]** These dyes or pigments may be added to the recording layer preferably in a proportion of 0.01 to 50% by weight, preferably 0.5 to 10% by weight in the case of the dye and 1.0 to 10% by weight in the case of the pigment, relative to the total solid component of the radical polymerization layer. When the added amount of pigment or dye is less than 0.1wt.%, the effect of sensitization becomes insufficient. When the added amount of pigment or dye exceeds 50wt.%, contamination is generated at non-image portions at the time of printing.

#### Other Compounds

**[0110]** As long as the object of the present invention is not compromised, various additives that may be used together with conventionally known photopolymerizable compounds can be appropriately used in the radical polymerization layer.

**[0111]** Examples of the additive include thermal polymerization inhibitors. Specifically, examples include quinones and phenol based compounds such as hydroquinone, pyrogallol, p-methoxyphenol, catechol, β-naphthol and 2,6-di-t-butyl-p-cresol. These compounds may be used in a proportion of 10 parts by weight, preferably in a proportion of about

0.01 to 5 parts by weight, relative to 100 parts by weight of the total, combined amount of the polymerizable compound having ethylenic unsaturated bonds and the binder resin.

[0112] Examples of compounds that can be added as an oxygen quencher include the N,N-diaryalkylaniline derivatives disclosed at column 11 line 58 to column 12 line 35 of USP 4,772,541.

[0113] A plasticizer may be also used to improve film quality. Examples include phthalic acid esters, trimellitic acid esters, adipic acid esters, other saturated or unsaturated carboxylic acid esters, citric acid esters, epoxylated soy bean oil, epoxylated linseed oil, epoxylated stearic acid, orthophosphoric acid esters, phosphonic acid esters and glycol esters.

[0114] It is also preferable to use an acid generator together that generates an acid by heating as an additive to accelerate the decomposition of the radical generator. Acid generators described later in detail in the description of the acid cross-linking layer may be used.

[0115] The radical polymerization layer may be formed by appropriately selecting respective components, dissolving the components in an appropriate solvent, and then coating the solvent on a support. However, the coating amount after drying is preferably about 1g/m<sup>2</sup> to 5.0g/m<sup>2</sup>.

[0116] When the infrared absorber is added to the radical polymerization layer, it is preferable to add the infrared absorber so that the optical density in a recording wavelength is in a range of 0.5 to 3. The radical generator, the polymerizable compound and the infrared absorber added if desired may be localized in microcapsules for the purpose of improving sensitivity. The microcapsules used herein preferably have a heat responsive property (i.e., internal materials are discharged upon heating during exposure). A method for forming such microcapsules is disclosed in detail in Japanese Patent Application Laid-Open (JP-A) No. 1-145190.

[0117] An overcoat layer impermeable to oxygen may be provided adjacent to the radical polymerization layer, in order to prevent polymerization inhibition oxygen. Preferable examples of materials for the overcoat layer include water soluble resins such as polyvinyl alcohol, carboxymethyl cellulose, hydroxyethyl cellulose, methyl cellulose and polyvinyl pyrrolidone. A film thickness of about 0.2 to 3 μm is appropriate.

#### Acid Catalyzed Decomposition

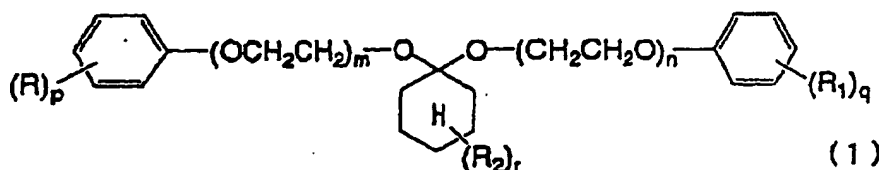
[0118] A chemical amplification layer is preferably formed at the exposure surface of the uppermost layer of the recording layer. The chemical amplification layer must have as components thereof a compound that generates an acid by the action of light or heat (i.e., an acid generator), and a compound whose chemical bonds are split by the acid generated as a catalyst and whose solubility in the alkali developing solution is thereby increased (an acid degradable compound).

[0119] The chemical amplification layer may also have a polymer compound that is a binder component for forming the layer. The acid degradable compound itself may be a polymer compound or a precursor that performs the function of the binder component.

#### Acid Degradable Compound

[0120] The compound whose solubility in the alkaline developer is raised by the dissociation of chemical bonds with an acid as a catalyst may also be called a compound having linking groups that may be decomposed in the molecule by an acid. The compound disclosed in Japanese Patent Application Laid-Open (JP-A) No. 9-171254 as "a compound having at least one bond decomposed by an acid" may be used for the purpose above. A preferable example of the chemical bond degradable by an acid is a  $-(CH_2CH_2O)_n-$  group (n represents an integer of 2 to 5).

[0121] Among these compounds, the compound represented by the general formula (1) below is preferably used from the standpoint of sensitivity and developability.



[0122] In the formula, R, R<sup>1</sup> and R<sup>2</sup> each represent a hydrogen atom, an alkyl group with a carbon number of 1 to 5, an alkoxy group with a carbon number of 1 to 5, a sulfo group, a carboxyl group or a hydroxyl group, p, q and r each

denote an integer of 1 to 3, and m and n each represent an integer of 1 to 5.

**[0123]** In the general formula (1), the alkyl group represented by R, R<sup>1</sup> and R<sup>2</sup> may be straight-chain or branched, and examples thereof include methyl, ethyl, propyl, isopropyl, butyl, t-butyl and pentyl groups. Examples of the alkoxy group include methoxy, ethoxy, propoxy, isopropoxy, butoxy, t-butoxy and pentoxy groups. The sulfo and carboxyl groups have salts of these groups. Compounds in which m and n are 1 or 2 are particularly preferable among the compounds represented by the general formula (1).

**[0124]** Examples of acid degradable compounds applicable to the present invention include the compounds having C-O-C bonds that are disclosed in Japanese Patent Application Laid-Open (JP-A) Nos. 48-89603, 51-120714, 53-133429, 55-12995, 55-126236 and 56-17345, the compounds having Si-O-C bonds that are disclosed in Japanese Patent Application Laid-Open (JP-A) Nos. 60-37549 and 60-121446, and other acid degradable compounds disclosed in Japanese Patent Application Laid-Open (JP-A) Nos. 60-3625 and 60-10247. The compounds having Si-N bonds disclosed in Japanese Patent Application Laid-Open (JP-A) No. 62-222246, the carbonate esters disclosed in Japanese Patent Application Laid-Open (JP-A) No. 62-251743, ortho-carbonate esters described in Japanese Patent Application Laid-Open (JP-A) No. 62-209451, the ortho-titanic acid esters disclosed in Japanese Patent Application Laid-Open (JP-A) No. 62-280841, the ortho-silicic acid esters disclosed in Japanese Patent Application Laid-Open (JP-A) No. 62-280842, the acetal, ketal and ortho-carboxylic acid esters disclosed in Japanese Patent Application Laid-Open (JP-A) Nos. 63-010153, 9-171254, 10-55067, 10-111564, 10-87733, 10-153853, 10-228102, 10-268507, 10-282648, 10-282670 and EP 0884547A1, and the compounds having C-S bonds that are disclosed in Japanese Patent Application Laid-Open (JP-A) No. 62-244038 may also be used.

**[0125]** The compounds having C-O-C and Si-O-C bonds, and the ortho-carbonate esters, acetals, ketals and silyl ethers disclosed in Japanese Patent Application Laid-Open (JP-A) Nos. 53-133429, 56-17345, 60-121446, 60-37549, 62-209451, 63-010153, 9-171254, 10-55067, 10-111564, 10-87733, 10-153853, 10-228102, 10-268507, 10-282648 and 10-282670, and in EP 0884647A1 are particularly preferable among the acid degradable compounds described above.

**[0126]** Among the foregoing acid degradable compounds, polymer compounds that have on the main chain thereof repeated acetal or ketal portions, and whose solubility in the alkali developing solution is raised by generated acids, are preferably used.

**[0127]** These compounds may be used singly, or in combination of two or more types. The compounds are added in the layer in a proportion of 5 to 70% by weight, preferably 10 to 50% by weight, and more preferably 15 to 35% by weight, relative to the total solid component of the chemical amplification layer. When the amount is less than 5% by weight, the non-image portions are easily contaminated. When the amount of addition exceeds 70% by weight, film strength of the image portions becomes insufficient.

**[0128]** Heat sensitive, positive-type acid degradable compounds may be used as the infrared absorber, and compounds similar to those described below may be used as the acid generator.

**[0129]** In the present invention, by a compound that generates an acid by light or heat (i.e., the acid generator) is meant a compound that is decomposed by being irradiated with infrared light or by being heated at a temperature of 100°C or higher to generate an acid. The acid generated is preferably a strong acid with a pKa value of 2 or less, such as sulfuric acid and hydrochloric acid.

**[0130]** Examples of acid generators favorably used in the present invention include onium salts such as iodonium salts, sulfonium salts, phosphonium salts and diazonium salts. Specifically, the compounds disclosed in USP 4,708,925 and Japanese Patent Application Laid-Open (JP-A) No. 7-20629 may be used. In particular, iodonium salts, sulfonium salts and diazonium salts having sulfonic acid ions as counterions are preferable. Examples of preferable diazonium salts include the diazonium compounds disclosed in USP 3,867,147, the diazonium compounds described in USP 2,632,703, and the diazo resins disclosed in Japanese Patent Application Laid-Open (JP-A) Nos. 1-102456 and 1-102457. The benzyisulfonates disclosed in USP 5,135,838 and USP 5,200,544 are also preferable. Activated sulfonic acid esters and disulfonyl compounds disclosed in Japanese Patent Application Laid-Open (JP-A) Nos. 2-100054 and 2-100055, and in Japanese Patent Application No. 8-9444, are also preferable. Further, the S-triazines substituted with haloalkyl groups disclosed in Japanese Patent Application Laid-Open (JP-A) No. 7-271029 are also preferable.

**[0131]** These compounds may be used singly, or in combination of two or more. Since the acid generators described above may be decomposed by ultraviolet irradiation, images can be recorded not only by infrared light irradiation but also by UV irradiation using the recording layer having such an embodiment.

**[0132]** In addition to there, various compounds may be added as necessary to the image recording layer of the planographic printing plate of the present invention.

**[0133]** For example, dyes having a large absorption at the visible region may be used as image coloring agents. Examples of these dyes include oil yellow #101, oil yellow #103, oil pink #312, oil green BG, oil blue BOS, oil blue #603, oil black BY, oil black BS and oil black T-500 (made by Orient Chemical Industry, Co.); victoria pure blue, crystal violet, (CI 42555), methyl violet (CI 42535), ethyl violet, rhodamin B (CI 145170B), malachite green (CI 42000), methylene blue (CI 52015) and eizenspiro blue C-RH (made by Hodogaya Chemicals Co.); and the dyes disclosed in

Japanese Patent Application Laid-Open (JP-A) No. 62-293247.

**[0134]** It is preferable to add these dyes since the distinction between image portions and non-image portions gains clarity after the formation the images. The amount of addition is preferably in the range of 0.01 to 10% by weight relative to the total solid fraction of the recording layer.

**[0135]** The nonionic surface active agents disclosed in Japanese Patent Application Laid-Open (JP-A) Nos. 62-25740 and 3-208514, and the amphoteric surface active agents disclosed in Japanese Patent Application Laid-Open (JP-A) Nos. 59-121044 and 4-13149 may be added in the recording layer of the present invention in order to raise the stability of processing under developing conditions. Examples of the nonionic surface active agent include sorbitan tristearate, sorbitan monopalmitate, sorbitan triolate, stearic acid monoglyceride, and polyoxyethylene nonylphenyl ether. Examples of the amphoteric surface active agent include alkyl-di(aminoethyl)glycine, alkyl polyaminoethyl glycine, 2-alkyl-N-carboxyethyl-N-hydroxyethyl imidazolium betaine, and N-tetradecyl-N,N-betaine type surface active agents (for example, Amogen (trade name), made by Dai-ichi Kōgyō Co.).

**[0136]** The ratio of the non-ionic and amphoteric surface active agents in the recording layer are preferably 0.05 to 15% by weight, more preferably 0.1 to 5% by weight.

**[0137]** It is preferable to adsorb a heat amplifier such as the metal powders and metal compound powders below to the photosensitive layer, the heat-insulating layer or the support surface in order to amplify heat generation.

**[0138]** The metal powders and metal compound powder will be described. By metal compound is meant a compound such as a metal, a metal oxide, a metal nitride, a metal sulfide or a metal carbide.

**[0139]** Examples of the metal compound includes such metals as Mg, Al, Si, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Y, Zr, Nb, Mo, Tc, Ru, Pd, Ag, Cd, In, Sn, Sb, Hf, Ta, W, Re, Os, Ir, Pt, Au and Pb. Among these, metals that readily induce exothermic reactions such as an oxidation reaction by heat energy are preferable. Specific examples include Al, Si, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Mo, Ag, Sn and W. Metals having a high radiation absorbing efficiency and exhibiting large self-heating exothermic reaction such as Fe, Co, Ni, Ti and Zr are preferable among them.

**[0140]** The metal compounds may be of one metal only, or two or more components, or may be structured of a metal and a metal oxide, nitride, sulfide or carbide. The self-activated thermal reaction thermal energy generated by such as oxidation is larger with an individual metal, but there is the danger of spontaneous combustion when the metal makes contact with air, since handling in air is complicated. Accordingly, it is preferable that the surface of such metal is covered with an oxide, nitride, sulfide or carbide to a depth of several nanometers from the surface.

**[0141]** The surface coating layer may be particles or a thin film such as a deposition film, but particles are preferable when the layer is formed together with an organic substance. The particle size is 10  $\mu\text{m}$  or less, preferably 0.005 to 5  $\mu\text{m}$ , and more preferably 0.01 to 3  $\mu\text{m}$ . When the particle size is 0.01  $\mu\text{m}$  or less, dispersion of the particles is difficult. When the particle size is 10  $\mu\text{m}$  or more, resolution of printed images deteriorates.

**[0142]** Iron powder is preferable among the metal fine powders of in the present invention. An iron alloy powder mainly composed of  $\alpha\text{-Fe}$  is more preferable among the preferable iron powders. These powders may have such atoms as Al, Si, S, Sc, Ca, Ti, V, Cr, Cu, Y, Mo, Rh, Pd, Ag, Sn, Sb, Te, Ba, Ta, W, Re, Au, Hg, Pb, Bi, La, Ce, Pr, Nd, P, Co, Mn, Zn, Ni, Sr and B, in addition to predetermined atoms. It is preferable that the powder has at least one of Al, Si, Ca, Y, Ba, La, Nd, Co, Ni and B, more preferably at least one of Co, Y and Al, in addition to  $\alpha\text{-Fe}$ . The content of Co relative to the content of Fe is preferably zero atomic % or more and to 40 atomic % or less, further preferably 15 atomic % or more and 35 atomic % or less, and more preferably 20 atomic % or more and 20 atomic % or less. The content of Y is preferably 1.5 atomic % or more and to 12 atomic % or less, further preferably 3 atomic % or more and 10 atomic % or less, and more preferably 4 atomic % or more and 9 atomic % or less. The content of Al is preferably 1.5 atomic % or more and to 12 atomic % or less, further preferably 3 atomic % or more and 10 atomic % or less, and more preferably 4 atomic % or more and 9 atomic % or less. The iron alloy fine powder may have a small amount of oxides or hydroxides. Specific examples are disclosed in Japanese Patent Application Publication (JP-B) Nos. 44-14090, 45-18372, 47-22062, 47-22513, 46-28466, 46-38755, 47-4286, 47-12422, 47-17284, 47-18509, 47-18573, 39-10307 and 46-39639, and USP 3,026,26215, 3,031,341, 3,100,194, 3,242,005 and 3,389,014.

**[0143]** These heat amplifiers are preferably used in a ratio of 0.01 to 50% by weight, more preferably 0.1 to 10% by weight, relative to the total solid fraction of the heat-insulating layer or recording layer. The amplification effect becomes insufficient when the amount of addition is less than 0.01% by weight. When the amount exceeds 50% by weight, film strength at the time of printing decreases.

**[0144]** The support that can be favorably used for the planographic printing plate of the present invention will be described.

**[0145]** A dimensionally stable plate may used as the support. Examples thereof include paper, paper laminated with a plastic (for example polyethylene, polypropylene and polystyrene), a metal plate (for example aluminum, zinc and copper), a plastic film (for example cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose butylate, cellulose acetate butylate, cellulose nitrate, polyethylene terephthalate, polyethylene, polystyrene, polypropylene, polycarbonate, and polyvinyl acetal), or paper or a plastic film on which foregoing metals are laminated or deposited.

**[0146]** Polyester film, or a plastic film on which aluminum is laminated or deposited, is particularly preferable as a

heat-insulation support having a low thermal conductivity and a high heat-insulation effect among the supports described above. The thickness of the support is in the range of 0.05 to 5.0 mm, preferably in the range of 0.05 to 2.0 mm, as described previously. Dimensional accuracy becomes poor when the thickness is smaller than 0.05 mm. When the thickness is larger than 5.0 mm, flexural strength is insufficient when the plate is wound on a printing machine, thereby causing cracks in the support itself. An aluminum plate is particularly preferable as a support having heat-insulation effect, since it is cheap and has excellent dimensional stability. A suitable aluminum plate may be an alloy plate having as main components a pure aluminum plate and aluminum, with a minute amount of foreign elements.

**[0147]** The foreign elements contained in the aluminum alloy may be silicon, iron, manganese, magnesium, chromium, zinc bismuth, nickel and titanium. The total amount of the foreign elements in the alloy is 10% by weight or less. While pure aluminum is favorable in the present invention, a minute amount of the foreign elements may be contained in aluminum, since production of perfectly pure aluminum is difficult in view of refining technology. The composition of the aluminum plate to be used in the present invention is not particularly restricted, and aluminum plates of conventionally known and used material may be appropriately used. The aluminum plate to be used in the present invention has a thickness of about 0.1 to 0.6 mm, preferably 0.15 to 0.4 mm, and a thickness of 0.2 to 0.3 mm is particularly preferable.

**[0148]** Prior to roughening the surface of the aluminum plate, a degreasing treatment with a surfactant, an organic solvent, or an alkaline water solution may be administered to the aluminum plate in order to eliminate rolling oil on the surface as needed.

**[0149]** The surface of the aluminum plate may be roughened in accordance with various methods. Examples thereof include a method in which the surface is mechanically roughened, a method in which the surface is electrochemically dissolved and roughened, and a method in which the surface is chemically roughened by selectively dissolving the surface. Methods such as ball polishing, brush polishing, blast polishing and buff polishing methods may be used for the mechanical roughening method. Examples of the electrochemical roughening method include a method in which an alternating current or a direct current is passed through an electrolytic solution of hydrochloric acid or nitric acid. A method in which both may be also used, as disclosed in Japanese Patent Application Laid-Open (JP-A) No. 54-63902.

**[0150]** Following alkaline etching and neutralization processing as needed, the aluminum plate thus roughened may be subjected to anodic oxidation as desired in order to raise the water retention and wear resistance of the surface. Various electrolytes that form a porous oxidation film can be used for the anodic oxidation of the aluminum plate, and sulfuric acid, phosphoric acid, citric acid, chromic acid or a mixed acid thereof may be used for that purpose. The concentration of the electrolyte is appropriately determined depending on the kind of the electrolyte.

**[0151]** After the anodic oxidation treatment has been administered, the aluminum surface may be subjected to a hydrophobic treatment as needed. The alkali metal silicate (for example, an aqueous solution of sodium silicate) methods disclosed in USP 2,714,066, 3,181,461, 3,280,734 and 3,902,734 can be used for the hydrophobic treatment applicable in the present invention. In these methods, the support is dipped in an aqueous sodium silicate solution or subjected to an electrolytic treatment. Other methods include the methods in which the aluminum surface is treated with potassium fluorozirconic acid as disclosed in Japanese Patent Application Publication (JP-B) No. 36-22063, and the method in which the aluminum surface is treated with polyvinyl sulfonic acid as disclosed in USP 3,276,868, 4,153,461 and 4,689,272.

**[0152]** The planographic printing plate of the present invention thus obtained is preferably recorded by an infrared laser.

**[0153]** The negative-type recording layer in the planographic printing plate of the present invention is subjected to developing processing with water or an alkaline developing solution after exposure. Because the heat-insulating intermediate layer or the heat-insulating support, which are the distinctive structures of the present invention, have the feature that they become hydrophilic by the alkaline developing solution, the effect of the present invention is most optimally displayed when an alkaline developing processing is administered.

**[0154]** The developing processing may be performed immediately after exposure, or a heat treatment may be performed between the exposure step and development step. When a heat treatment is administered, it is preferable that the temperature is within a range of 60°C to 150°C and that the heat treatment is conducted for 5 seconds to 5 minutes. Various, conventionally known methods may be employed. Examples thereof include a method in which the recording materials are heated by a panel heater or a ceramic heater while the heater is brought into contact with the recording materials, and a method in which the recording materials are heated by a lamp or warm air without contact. These heating treatment; allow the laser energy required for recording at the time of irradiation to be reduced.

**[0155]** When an alkaline water solution is used, conventionally known as alkaline water-solutions may be used as the developing solution and replenisher. Examples include inorganic alkaline salts such as sodium or potassium silicate; sodium, potassium or ammonium phosphate, sodium, potassium or ammonium hydrogen phosphate; sodium, potassium or ammonium carbonate; sodium, potassium or ammonium hydrogen carbonate; sodium, potassium or ammonium borate, and sodium, ammonium, potassium or lithium hydroxide. Organic alkaline salts may be also used, including monomethylamine, dimethylamine,



trimethylamine, monoethylamine, diethylamine, triethylamine, monoisopropylamine, diisopropylamine, triisopropylamine, n-butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, isopropanolamine, ethyleneimine, ethylenediamine and pyridine.

**[0156]** These alkaline chemicals may be used singly, or in combination of two or more.

5 **[0157]** Among these alkali agents, an aqueous silicate salt solution such as sodium silicate and potassium silicate is particularly preferable because developability can be adjusted depending on the ratio and concentration of silicon oxide  $\text{SiO}_2$  and alkali metal oxide  $\text{M}_2\text{O}$  (M denotes an alkali metal), which are components of the silicate. For example, the silicates of alkali metals as disclosed in Japanese Patent Application Laid-Open (JP-A) No. 54-62004 and Japanese Patent Application Publication (JP-B) No. 57-7427 may be effectively used.

10 **[0158]** Further, when an automatic developing machine is used for development, it is known that a large amount of recording layers can be processed without changing developing solutions in the developing tank over a long period of time by adding to the developing solution an aqueous solution whose alkaline strength is greater than that of the developing solution. This supplement method may be preferably used in the present invention.

15 **[0159]** The recording layer developed using the developing solution and replenisher described above is washed with water, and post-treated with a rinse liquid having a surface active agent and the like, and a non-sensitizing grease solution having gum arabic or starch derivatives. A variety of these post-treatments may be combined as post-treatments when the planographic printing plate of the present invention is used in printing.

**[0160]** In recent years, automatic developing machines for plate materials in printing have come to be used widely, particularly in the plate-making and printing industries, because of the rationalization and standardization of plate-making labor.

20 **[0161]** The automatic developing machine usually has a development part and post-processing part, a device for conveying printing plates, processing fluid tanks and a spray device. A printing plate once exposed is sprayed with various processing fluids that have been drawn up by pumps and sprayed out from spray nozzles while the plate is conveyed horizontally, whereby developing processing is carried out. Recently, a method has come to be known in which printing materials are dipped and conveyed by guide rolls in processing fluid tanks filled with processing fluids. In this type of automated processing, processing can be carried out by replenishing the various processing fluids with replenishing fluids in accordance with processing amount, operation time and the like.

**[0162]** A so-called disposable processing method in which substantially fresh processing fluids are used may be also employed.

30 **[0163]** The planographic printing plate thus obtained may be ready for the printing step after being coated with a non-sensitizing grease gum, as desired. A burning treatment may also be administered for the purpose of further improving tolerance to repeated printings.

**[0164]** When the planographic printing plate is burned, it is preferably treated with the surface adjustment liquid as disclosed in Japanese Patent Application Publication (JP-B) Nos. 61-2518 and 55-28062 and Japanese Patent Application Laid-Open (JP-A) Nos. 62-31859 and 61-159655.

35 **[0165]** The planographic printing plate coated with the surface adjustment liquid is dried, if necessary, and is heated at a high temperature with a burning processor (for example, a burning processor BP-1300 available from Fuji Photo Film Co.). The heating temperature and time are preferably 180 to 300°C and 1 to 20 minutes, respectively, although they depend on the type of components forming the image.

40 **[0166]** The planographic printing plate that has been subjected to the burning treatment may be appropriately subjected to conventional treatments such as washing and coating with a gum. However, the so-called non-sensitizing grease treatment such as gum coating may be omitted when a surface adjustment liquid having a water soluble polymer compound is used.

45 **[0167]** The planographic printing plate obtained by such treatments as described above is placed on an offset printing machine, and used for a number of printings.

## EXAMPLES

50 **[0168]** The present invention will hereinafter be described in detail with reference to Examples. However, the present invention is not limited to the same.

### *Preparation of Support A: Support That is Not a Heat-Insulating Material, Example 1*

55 **[0169]** An aluminum plate (material 1050) having a thickness of 0.30mm was cleansed with trichloroethylene and degreased. The surface of the aluminum plate was then grained using a nylon brush and an aqueous suspension of 400 mesh permestone, and thoroughly washed with water. The aluminum plate was dipped into a 25% aqueous solution of sodium hydroxide for 9 seconds, etched, washed, then further dipped into a 2% aqueous solution of  $\text{HNO}_3$  for 20 seconds and washed. The etching amount of the grained surface at this time was about  $3\text{g/m}^2$ . Next, using 7%  $\text{H}_2\text{SO}_4$

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as an electrolyte, the plate was disposed with a direct current anodic oxidized film of  $3\text{g/m}^2$  at an electric current density of  $15\text{A/dm}^2$ . The plate was then washed and dried.

### *Preparation of Support B: Support That is Not a Heat-Insulating Material, Example 2*

**[0170]** The support A was dipped in a silicate solution described below at  $35^\circ\text{C}$ . The support was then dried at  $30^\circ\text{C}$  for 1 minute, washed and dried to form a silicate surface.

(silicate solution)

**[0171]** #3 sodium silicate 2.5g  
pure water 100g

### *Preparation of Support C: Heat-Insulating Material Support, Example 1*

**[0172]** A commercially available polyethylene terephthalate support having a thickness of 0.2mm.

### *Preparation of Hydrophilic, Heat-Insulating Supports 1-9: Table 10*

**[0173]** Using a wire bar, the following cross-linked hydrophilic layers were coated on supports selected from the supports A, B and C, and dried to obtain heat-insulating supports having hydrophilic layers.

**[0174]** Details of the supports used, the hydrophilic layers formed, and film thickness of the layers are shown in Table 10.

Table 10

Heat-insulating support	Substrate used	Cross-linked hydrophilic layer	Film thickness of hydrophilic layer ( $\mu\text{m}$ )	Film forming conditions
1	Substrate A	Hydrophilic layer A	1.0	100 °C, 10 minutes
2	Substrate A	Hydrophilic layer E	1.0	100 °C, 10 minutes
3	Substrate A	Hydrophilic layer F	1.0	100 °C, 10 minutes
4 (Adhesive added)	Substrate A	Hydrophilic layer F2	0.5	100 °C, 10 minutes
5	Substrate B	Hydrophilic layer A	1.0	100 °C, 10 minutes
6	Substrate B	Hydrophilic layer B	1.0	100 °C, 10 minutes
7	Substrate B	Hydrophilic layer C	1.0	100 °C, 10 minutes
8	Substrate B	Hydrophilic layer D	1.0	100 °C, 10 minutes
9 (Adhesive added)	Substrate B	Hydrophilic layer E2	1.0	100 °C, After drying for 1 minute
10	Substrate C	Hydrophilic layer E	0.5	Uv exposure of whole surface (1000 counts)
11 (Adhesive added)	Substrate C	Hydrophilic layer E2	0.5	(Aitolary printer, made by ai graphic co.) 100 °C, 10 minutes 100 °C, 10 minutes 100 °C, 10 minutes

## (1) Hydrophilic Layer A Coating Solution

**[0175]** A mixed solution of 200g of colloidal silica (trade name: Snowtechs R503, 20wt.% aqueous dispersion solution, made by Nissan Chemical Industries, Co.) and 5g of aminopropyl triethoxy silane.

## (2) Hydrophilic Layer B Coating Solution

**[0176]** Dispersed for 30 minutes with glass beads in a paint shaker (made by Tōyō Precision Machine Co.) were 50g of titanium oxide (made by Titan Industries Co., particle size  $0.3\mu$ ), 113g of 10% aqueous polyvinyl alcohol (trade name: PVA 117, made by Kurarey Co.) and 240g of water. Further, 110g of 20% solution (water/ethanol = 1/1 in weight ratio) of tetraethoxysilane previously hydrolyzed with phosphoric acid and 200g of colloidal silica (trade name: Snowtechs R503, 20% aqueous dispersion solution, made by Nissan Chemical Industries, Co.) were added and, after dispersing for 3 minutes, a dispersion solution was obtained by filtering the glass beads off.

## (3) Hydrophilic Layer C Coating Solution

**[0177]** The same solution was obtained, except that Fe particles were used in place of titanium oxide in the hydrophilic layer B coating solution.

**[0178]** A fine powder of an iron alloy with a Fe : Co : Al : Y ratio of 100 : 20 : 5 : 5, longitudinal diameter of  $0.1\mu$ , transverse diameter of  $0.02\mu$  and specific surface area of  $60\text{ m}^2/\text{g}$  were used.

## (4) Hydrophilic Layer D Coating Solution

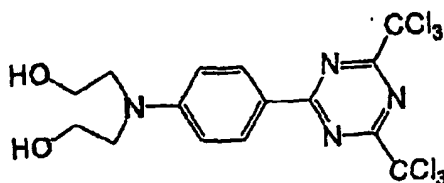
*Preparation of Hydrophilic Polymer*

**[0179]** Polyacrylic acid (18.0g, molecular weight 25,000, made by Wako Pure Chemicals Co.) was dissolved in dimethyl acetoamide, and the solution was allowed to react for 3 hours after adding 5.5g of 2-methacryloyl oxyethyl isocyanate (abbreviated as MOI hereinafter) and 0.1g of dibutyl tin dilaurate. Then, 20% equivalent of the carboxylic group was partially neutralized with sodium hydroxide, and the polymer was precipitated by adding acetone to obtain a purified hydrophilic polymer P-1 by thorough washing. Then, a solution was obtained by dissolving 1.10g of the hydrophilic polymer P-1, 0.1g of a triazine initiator described below, 0.5g of polyethyleneglycol diacrylate (A600, made by Toa synthetic Chemicals Co.) and 2.5g of dipentaerythritol diacrylate in a mixed solvent of 10g of methanol and 10g of water.

**[0180]** The structure of the triazine initiator A is shown below.

## Triazine initiator A

**[0181]**



## (5) Hydrophilic Layer E Coating Solution

**[0182]** A solution was obtained by dissolving 100g of polyvinyl alcohol (trade name PVA 117, made by Kurarey Co.) in 200g of water, followed by adding 300g of a 30% solution of tetraethoxysilane (water/ethanol = 1/1 weight ration) previously hydrolyzed with phosphoric acid.

## (6) Hydrophilic Layer F Coating Solution

**[0183]** A solution was obtained by adding 50g of a 30% tetramethoxysilane solution into 100g of 50wt.% aqueous

solution of #3 sodium silicate.

(7) Hydrophilic Layer E2 Coating Solution (coating solution containing an adhesive; used for further laminating a radical polymerisation layer thereon)

**[0184]** A solution was obtained by dissolving 100g of a 10% aqueous solution of polyvinyl alcohol (trade name PVA 117, made by Kurarey Co.) in 200g of water, followed by adding 300g of a 30% mixed solution (water/methanol = 2/1 weight ratio) of [(3-methacryloxypropane trimethoxysilane previously hydrolyzed with phosphate catalyst) / (tetramethoxysilane) = 50/50 wt.%].

(8) Hydrophilic Layer F2 Coating Solution (coating solution containing an adhesive; used for further laminating a radical polymerisation layer thereon)

**[0185]** A solution was obtained by adding 50g of a 30% methanol solution of a mixture of [(3-methacryloxypropane trimethoxysilane)/tetramethoxysilane- 50/50 wt.%] in 100g of 50 wt% aqueous solution of #3 sodium silicate.

*Preparation of Heat-Insulating Support Capable of Being Made*

*Hydrophilic: Treatment with an Adhesive (Table 11)*

**[0186]** The heat-insulating support that is capable of being made hydrophilic (i.e., the heat support of the present invention) was obtained by using a wire bar to coat the following adhesives on supports selected from the above hydrophilic heat-insulating supports 1 through 11.

**[0187]** The supports and adhesives that were used, and the conditions in which the adhesive layers were formed, are shown in Table 11.

Table 11

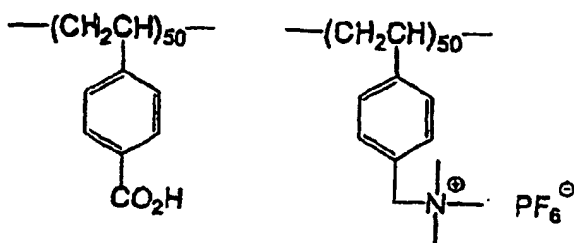
Substrate	Heat insulation support used	Adhesive layer	Adhesive layer coating agent(mg/m <sup>2</sup> )	Film-forming conditions	Contact angle (in degrees)
1	Substrate 1	Adhesive A	70	100 °C, 1 minute	50
2	Substrate 2	Adhesive C	50	100 °C, 5 minutes	30
3	Substrate 3	Adhesive D	100	100 °C, 1 minute	55
4	Substrate 4	None	50	100 °C, 1 minute	20
5	Substrate 5	Adhesive B	80	100 °C, 10 minutes	50
6	Substrate 6	Adhesive A	70	100 °C, 1 minute	60
7	Substrate 7	Adhesive B	80	100 °C, 10 minutes	55
8	Substrate 8	Adhesive A	70	100 °C, 1 minute	55
9	Substrate 9	None	---		20
10	Substrate 10	Adhesive C	50	100 °C, 5 minutes	30
11	Substrate 11	None	---		25
12	Substrate 3	Adhesive E	80	100 °C, 10 minutes	60
13	Substrate 5	Adhesive E	80	100 °C, 10 minutes	65
14	Substrate 7	Adhesive E	80	100 °C, 10 minutes	60

## (1) Adhesive A Coating Solution

**[0188]** A 5wt.% methanol solution of an adhesive polymer A with the structure described below, obtained by radical polymerization.

Adhesive polymer A

**[0189]**



## (2) Adhesive B Coating Solution

**[0190]** 3-methacryloxypropyl trimethoxysilane (1.4g), tetramethoxysilane (4.0g), phosphoric acid (1.4g) and water (1.5g) were stirred at room temperature for 1 hour, and diluted with methanol to a solution with a final concentration of 5 wt%.

## (3) Adhesive C Coating Solution

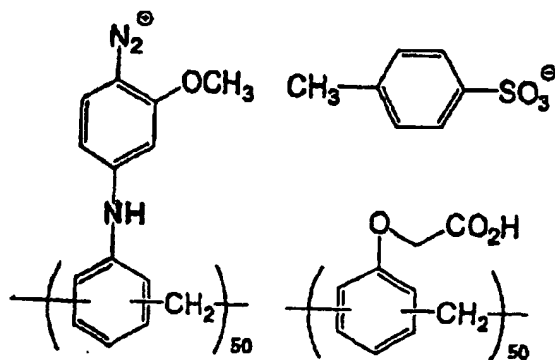
**[0191]** A mixed solution of phenylboric acid/5% methanol solution of boric acid/water (weight ratio 2/8).

## (4) Adhesive D Coating Solution

**[0192]** A 5 wt.% methanol solution of a formaline condensation polymerization product D of an azonium salt shown by the following structure.

Diazonium salt condensation polymerisation product D

**[0193]**



## (5) Adhesive E Coating Solution

**[0194]** A phenol resin E (1.5g) with the structure below, tetramethoxysilane (4.0g), sulfuric acid (1.0g) and water

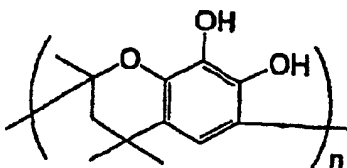
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(1.5g) were stirred at room temperature for 1 hour, and diluted with methanol in a solution with a final concentration of 5 Wt%.

Phenol Resin E

pyrogallol/acetone condensation product

**[0195]**



*Preparation of Comparative Support*

**[0196]** Using the supports made for the Examples, the following comparative supports were made without forming adhesive layers or administering treatments to improve adhesion.



Table 12

Comparative support	Support used	Contact angle (in degrees)
Comparative example 1	Hydrophilic heat insulation support 1	~0 (Expanding wetting)
Comparative example 2	Hydrophilic heat insulation support 2	~0 (Expanding wetting)
Comparative example 3	Hydrophilic heat insulation support 3	~0 (Expanding wetting)
Comparative example 4	Without contact agent in forming heat insulation support 4	~0 (Expanding wetting)
Comparative example 5	Hydrophilic heat insulation support 5	~0 (Expanding wetting)
Comparative example 6	Hydrophilic heat insulation support 6	~0 (Expanding wetting)
Comparative example 7	Hydrophilic heat insulation support 7	~0 (Expanding wetting)
Comparative example 8	Hydrophilic heat insulation support 8	~0 (Expanding wetting)
Comparative example 9	Without contact agent in forming heat insulation support 9	~0 (Expanding wetting)
Comparative example 10	Hydrophilic heat insulation support 10	~0 (Expanding wetting)
Comparative example 11	Without contact agent in forming heat insulation support 11	~0 (Expanding wetting)
Comparative example 12	Substrate A	30
Comparative example 13	Substrate B	~0 (Expanding wetting)
Comparative example 14	Substrate C	70
Comparative example 15	Contact agent A was directly coated on the support A to a thickness of 70 mg/m <sup>2</sup>	30
Comparative example 16	Contact agent C was directly coated on the support A to a thickness of 50 mg/m <sup>2</sup>	40
Comparative example 17	Contact agent D was directly coated on the support A to a thickness of 100 mg/m <sup>2</sup>	35
Comparative example 18	Contact agent A was directly coated on the support B to a thickness of 70 mg/m <sup>2</sup>	10
Comparative example 19	Contact agent B was directly coated on the support B to a thickness of 70 mg/m <sup>2</sup>	15
Comparative example 20	Contact agent C was directly coated on the support C to a thickness of 50 mg/m <sup>2</sup>	0
Comparative example 21	Contact agent E was directly coated on the support A to a thickness of 80 mg/m <sup>2</sup>	~0 (Expanding wetting)
Comparative example 22	Contact agent E was directly coated on the support B to a thickness of 80 mg/m <sup>2</sup>	10

*Examples 1 to 14, Comparative Examples 1 to 22**(Preparation of Lithographic Printing Plate: Coating of the Recording Layer)*

- 5 **[0197]** Ten kinds of coating solutions for the recording layer were prepared from the coating solutions 1 to 10. The cross-linking agents, polymers, acid generators, radical generators and Infrared absorbers used for these coating solutions are shown in Table 13. The structures of the compounds used are also shown below. The planographic printing plates 1 to 14 were obtained by coating on the supports 1 to 14 of the present invention the obtained coating solutions, and then allowing the coatings to dry at 100°C for 1 minute. The weight after drying was 1.5 g/m<sup>2</sup>. The planographic printing plates (Comparative Examples 1 to 22) were also prepared by providing the following recording layers using the comparative supports 1 to 22.

*Coating Solutions 1 to 3: Solutions for forming acid catalyst cross-linking layer (not according to the invention)*15 **[0198]**

- Cross-linking agent [X] in Table 13 0.5g
- Polymer [Y] in Table 13 1.5g
- Acid generator [Z] in Table 13 0.2g
- 20 • Infrared absorber [Q] in Table 13 0.15g
- Coloring agent (trade name: Aizen SPLON BLUE C-RH made by Hodogaya Chemical Co.) 0.015g
- Fluorinated surface active agent (trade name: Mefafax F-177 made by Dainihon Ink Chemical Industries Co.) 0.06g
- 25 • methylethyl ketone 15.0 g
- 1-methoxy-2-propanol 15.0g

*Coating Solution 4 to 7: coating solution for forming radical polymerization layer*30 **[0199]**

- arylmethacrylate/methacrylic acid = 70/30 copolymer (number average molecular weight 70,000) 1.2g
- dipentaerythritol hexaacrylate (DHPA, made by Nihon Kayaku Co.) 1.0g
- 35 • radicalgenerator [P] in Table 13 0.1g
- infrared absorber [Q] in Table 13 0.1g
- coloring agent (trade name; Victoria Pure Blue naphthalene sulfonic acid salt, made by Hodogaya Chemical Co.) 0.015g
- fluorinated surface active agent (trade name: Magafax F-176, Dainihon Ink Chemical Industries Co.) 0.06g
- 40 • methylethyl ketone 15.0g
- methanol 15.0g

*Coating Solutions 8 to 10: solutions for forming interaction release type positive layer (not according to the invention)*

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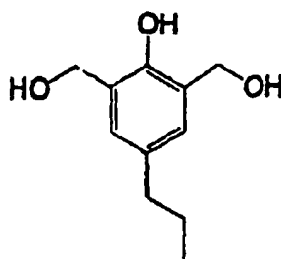
**[0200]**

- Polymer [Y] in Table 13 2.0g
- Infrared absorber [Q] in Table 13 0.15g
- 50 • Coloring agent (trade name: Aizen Splon Blue C-RH, made by Hodogaya Chemicals Co.) 0.015g
- Fluorinated surface active agent (trade name: Megafax F-177, made by Dai-nihon Ink Chemical Industries Co.) 0.06g
- methylethyl ketone 10.0g
- 55 • 1-methoxy-2-propanol 7.0g
- $\gamma$ -butyrolactone 10.0g

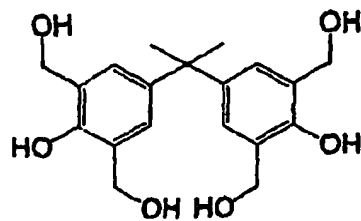
Table 13

	X	Y	Z	P	Q
Coating solution 1	X-1	Y-1	Z-1	None	Q-1
Coating solution 2	X-2	Y-2	Z-2	None	Q-2
Coating solution 3	X-3	Y-3	Z-1	None	Q-3
Coating solution 4	None	None	None	P-1	Q-1
Coating solution 5	None	None	None	P-2	Q-2
Coating solution 6	None	None	None	P-3	Q-3
Coating solution 7	None	None	None	P-1	Q-4
Coating solution 8	None	Y-1	None	None	Q-1
Coating solution 9	None	Y-2	None	None	Q-2
Coating solution 10	None	Y-3	None	None	Q-3

X-1



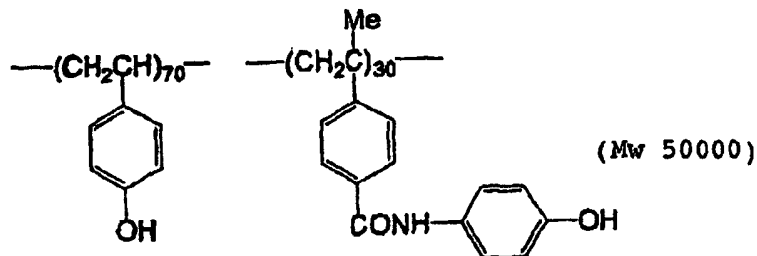
X-2



X-3 Resol resin (Mw 3000)

[0201]

Y-1

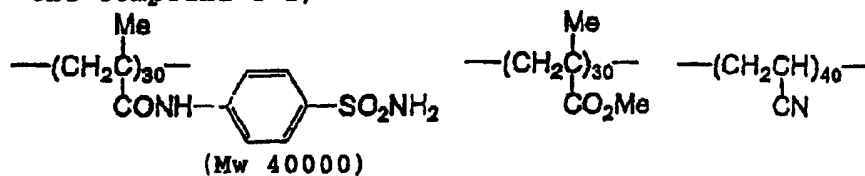


Y-2

[0202] Formaline condensation product (Noborac) with m-cresol/p-cresol = 60/40 (Mw 8000)

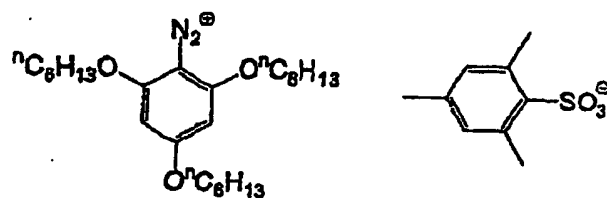
Y-3

the compound Y-2/

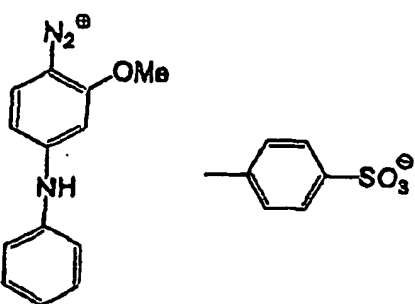


= 50% by weight/50% by weight mixture

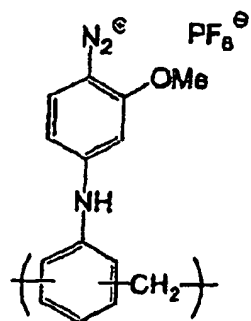
Z-1



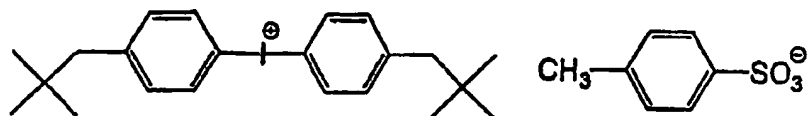
Z - 2



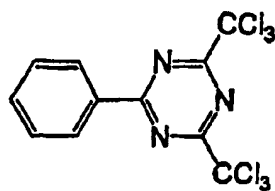
P - 1



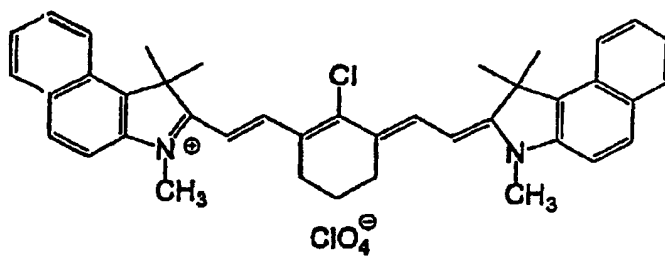
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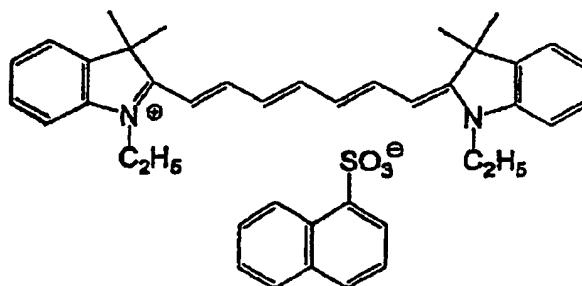
P - 3



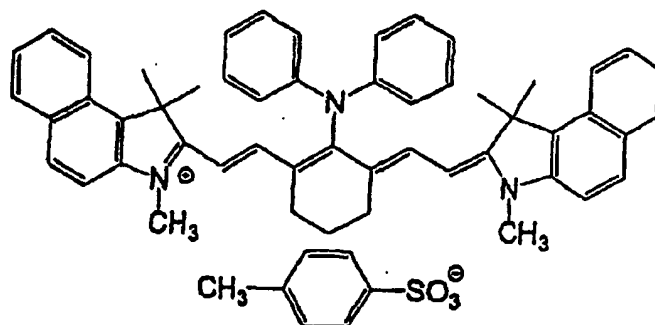
Q-1



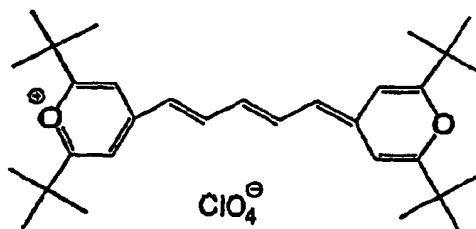
Q-2



Q-3



Q-4



*Evaluation of Sensitivity*

[0203] The planographic printing plate was exposed to and scanned with a semiconductor laser emitting an infrared light with a wave length of about 830 to 850 nm. After exposure, the acid cross-linking sensitive material (i.e., the recording layers of the coating solutions 5 to 8) were heated with a panel heater at 120°C for 30 seconds. The acid cross-linking sensitive material was then developed with a developing solution DP-4 (1:8 water dilution) made by Fuji Photo Film, Co. The amount of energy required for recording was calculated based on the line width of the image obtained, laser output loss in the optical system and scanning speed to serve as an index of sensitivity.

*Evaluation of Tolerance to Repeated Printings and Printing Contamination*

[0204] Using as printing plates planographic printing plates on which 1% mesh dots (highlights) had formed by exposure and development processing, the plates were printed with a Hydel KOR-D machine. The number of plates on which the mesh dots had been printed was used as an index for comparing tolerance to repeated printings. An index of 100 or higher was evaluated to be good and preferable from the standpoint of manufacturing. Printing contamination of non-image portions of the 100,000th plate of the printed plates was also inspected.

[0205] Evaluation results are shown in Tables 14 and 15.

Table 14

	Recording layer provided on the support (shown by the number of the coating solution)	Sensitivity (mJ/cm <sup>2</sup> )	Tolerance to repeated printings (index)	Printing contamination
Example 1*	Coating solution 1*	80	100	None
Example 2	4	90	100	None
Example 3*	8*	90	110	None
Example 4	5	65	110	None
Example 5*	2*	90	100	None
Example 6*	8*	85	105	None
Example 7	6	90	110	None
Example 8*	3*	80	110	None
Example 9	7	65	120	None
Example 10*	9*	75	105	None
Example 11	7	65	110	None
Example 12*	10*	80	110	None
Example 13*	8*	85	120	None
Example 14	6	85	120	None

\* not according to the invention

Table 15

	Recording layer provided on the support (shown by the number of the coating solution)	Sensitivity (mJ/cm <sup>2</sup> )	Tolerance to repeated printings (index)	Printing contamination
Comparative example 1	1	Effusion (poor adhesion)		
Comparative example 2	4	Effusion (poor adhesion)		
Comparative example 3	8	Effusion (poor adhesion)		
Comparative example 4	5	Effusion (poor adhesion)		
Comparative example 5	2	Effusion (poor adhesion)		
Comparative example 6	8	Effusion (poor adhesion)		
Comparative example 7	6	Effusion (poor adhesion)		
Comparative example 8	3	Effusion (poor adhesion)		
Comparative example 9	7	Effusion (poor adhesion)		
Comparative example 10	9	Effusion (poor adhesion)		
Comparative example 11	7	Effusion (poor adhesion)		
Comparative example 12	10	130	100	Contaminated
Comparative example 13	2	130	20	None
Comparative example 14	7	120	60	Contaminated
Comparative example 15	1	140	100	Contaminated
Comparative example 16	4	130	100	Contaminated
Comparative example 17	8	150	105	Contaminated
Comparative example 18	2	135	60	None
Comparative example 19	6	130	50	None
Comparative example 20	9	75	30	Contaminated
Comparative example 21	10	130	60	Contaminated
Comparative example 22	2	130	50	None



As shown in Tables 14 and 15, the planographic printing plate according to the present invention, in which one of a heat-insulating intermediate layer and a heat-insulating support is used, had excellent adhesion, high sensitivity, a high tolerance to repeated printings, and no contamination at the time of printing, regardless of the type of recording layer or the method of image formation. By contrast, with the planographic printing plates of the Comparative Examples, in which conventional supports were used that do not have the property of becoming hydrophilic even when a heat-insulating support is used and that were not subjected to an adhesion treatment, plates of high hydrophilicity displayed insufficient adhesion with the recording layer and generated image flow, and plates of high hydrophobicity displayed contamination in non-image portions due to a deterioration in the hydrophobicity, though some had adequate levels of tolerance to repeated printings.

[0206] According to the present invention, a planographic printing plate, of the type developed in alkaline water, can be provided which is sensitive to an infrared laser, reduces loss of exposure energy, can form an image in which image on/off is expanded in portions irradiated with an infrared laser and in portions not irradiated with an infrared laser, has high sensitivity, tolerance to repeated printings and excellent storage stability.

## Claims

1. An infrared-sensitive planographic printing plate comprising:

- (1) a support,
- (2) a first layer that has an average thickness of 0.05 to 50  $\mu\text{m}$  and is structured by a heat-insulating material having a thermal conductivity of  $3.0 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  or less, the surface of which can be made hydrophilic by being processed with one of an alkali and a silicate in an alkali developing solution after exposure; and
- (3) a second layer whose alkali developability is changed, without ablation, by being irradiated with an infrared ray, wherein this infrared-sensitive layer is a negative-type radical polymerisation recording layer; being sequentially laminated.

2. An infrared-sensitive planographic printing plate comprising:

- (1) a support that has an average thickness of 0.05 to 5.0 mm and is structured by a heat-insulating material having a thermal conductivity of  $3.0 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  or less, the surface of which can be made hydrophilic by being processed with one of an alkali and a silicate in an alkali developing solution after exposure; and
- (2) an infrared-sensitive layer whose alkali developability is changed by being irradiated with an infrared ray, wherein this infrared-sensitive layer is a negative-type radical polymerisation recording layer; being sequentially laminated.

3. A planographic printing plate according to claim 1, wherein the thermal conductivity of the heat-insulating material is  $1.0 \text{ (W}\cdot\text{m}^{-1}\cdot\text{K}^{-1})$  or less.

4. A planographic printing plate according to claim 2, wherein the thermal conductivity of the heat-insulating material is  $1.0 \text{ (W}\cdot\text{m}^{-1}\cdot\text{K}^{-1})$  or less.

5. A planographic printing plate according to claim 1, wherein the heat-insulating material is a crosslinked hydrophilic layer.

6. A planographic printing plate according to claim 5, wherein the heat-insulating material further comprised an adhesive.

7. A planographic printing plate according to claim 5, wherein the planographic printing plate comprises an adhesive layer between the first layer and the second layer.

8. A planographic printing plate according to claim 5, wherein the adhesiveness of the heat-insulating material is improved by regulating the balance between hydrophobicity and hydrophilicity of the heat-insulating material.

9. A planographic printing plate according to claim 1, wherein the radical polymerization recording layer comprises an infrared absorber.

10. A planographic printing plate according to claim 2, wherein the radical polymerization type recording layer com-

prises an infrared absorber.

11. A planographic printing plate according to claim 9, wherein the infrared absorber is one of an infrared absorber having an onium salt structure and an anionic infrared absorber.

12. A planographic printing plate according to claim 10, wherein the infrared absorber is one of an infrared absorber having an onium salt structure and an anionic infrared absorber.

## Patentansprüche

1. Infrarotempfindliche Flachdruckplatte, welche umfasst:

(1) einen Träger,

(2) eine erste Schicht mit einer mittleren Dicke von 0,05 bis 50  $\mu\text{m}$ , die aus einem wärmeisolierenden Material mit einer thermischen Leitfähigkeit von  $3,0 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$  oder weniger aufgebaut ist, deren Oberfläche durch Behandlung mit einem Alkali und/oder einem Silikat in einer Alkali-Entwicklerlösung nach dem Belichten hydrophil gemacht werden kann; und

(3) eine zweite Schicht, deren Alkali-Entwickelbarkeit sich - ohne Abtragung - durch die Bestrahlung mit Infrarotstrahlung ändert, wobei diese infrarotempfindliche Schicht eine radikalische Polymerisationsaufzeichnungsschicht vom negativen Typ ist;

wobei diese nacheinander laminiert sind.

2. Infrarotempfindliche Flachdruckplatte, welche umfasst:

(1) einen Träger mit einer mittleren Dicke von 0,05 bis 5,0 mm, die aus einem wärmeisolierenden Material mit einer thermischen Leitfähigkeit von  $3,0 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$  oder weniger aufgebaut ist, deren Oberfläche durch Behandlung mit einem Alkali und/oder einem Silikat in einer Alkali-Entwicklerlösung nach dem Belichten hydrophil gemacht werden kann; und

(2) eine infrarotempfindliche Schicht, deren Alkali-Entwickelbarkeit sich durch die Bestrahlung mit Infrarotstrahlung ändert, wobei diese infrarotempfindliche Schicht eine radikalische Polymerisationsaufzeichnungsschicht vom negativen Typ ist;

wobei diese nacheinander laminiert sind.

3. Flachdruckplatte gemäss Anspruch 1, worin die thermische Leitfähigkeit des wärmeisolierenden Materials  $1,0 \text{ (W}\cdot\text{m}^{-1}\text{K}^{-1})$  oder weniger beträgt.

4. Flachdruckplatte gemäss Anspruch 2, worin die thermische Leitfähigkeit des wärmeisolierenden Materials  $1,0 \text{ (W}\cdot\text{m}^{-1}\text{K}^{-1})$  oder weniger beträgt.

5. Flachdruckplatte gemäss Anspruch 1, worin das wärmeisolierende Material eine vernetzte hydrophile Schicht ist.

6. Flachdruckplatte gemäss Anspruch 5, worin das wärmeisolierende Material ferner einen Klebstoff umfasst.

7. Flachdruckplatte gemäss Anspruch 5, worin die Flachdruckplatte eine Klebstoffschicht zwischen der ersten Schicht und der zweiten Schicht umfasst.

8. Flachdruckplatte gemäss Anspruch 5, worin die Klebefähigkeit des wärmeisolierenden Materials durch Regulieren des Gleichgewichts zwischen Hydrophobie und Hydrophilie des wärmeisolierenden Materials verbessert wird.

9. Flachdruckplatte gemäss Anspruch 1, worin die radikalische Polymerisationsaufzeichnungsschicht einen Infrarotabsorber umfasst.

10. Flachdruckplatte gemäss Anspruch 2, worin die radikalische Polymerisationsaufzeichnungsschicht einen Infrarotabsorber umfasst.

5 11. Flachdruckplatte gemäss Anspruch 9, worin der Infrarotabsorber ein Infrarotabsorber mit einer Oniumsalzstruktur und/oder ein anionischer Infrarotabsorber ist.

12. Flachdruckplatte gemäss Anspruch 10, worin der Infrarotabsorber ein Infrarotabsorber mit einer Oniumsalzstruktur und/oder ein anionischer Infrarotabsorber ist.

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## Revendications

1. Plaque d'impression planographique sensible aux infrarouges comprenant :

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(1) un support,

(2) une première couche qui possède une épaisseur moyenne de 0,05 à 50  $\mu\text{m}$  et qui est structurée par un matériau calorifuge possédant une conductivité thermique de 3,0  $\text{Wm}^{-1}\text{K}^{-1}$  ou moins, dont la surface peut être rendue hydrophile en étant traitée avec l'un de un alcali et un silicate dans une solution développant un alcali après exposition ; et

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(3) une deuxième couche dont la capacité de développement de l'alcali est modifiée, sans ablation, en étant irradiée avec un rayon infrarouge, dans laquelle cette couche sensible aux infrarouges est une couche d'enregistrement à polymérisation par radicaux de type négatif ;  
qui est laminée séquentiellement.

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2. Plaque d'impression planographique sensible aux infrarouges comprenant :

(1) un support qui possède une épaisseur moyenne de 0,05 à 5,0 mm et qui est structuré par un matériau calorifuge possédant une conductivité thermique de 3,0  $\text{Wm}^{-1}\text{K}^{-1}$  ou moins, dont la surface peut être rendue hydrophile en étant traitée avec l'un d'un alcali et un silicate dans une solution développant un alcali après exposition ; et

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(2) une couche sensible aux infrarouges dont la capacité de développement de l'alcali est modifiée en étant irradiée avec un rayon infrarouge, dans laquelle cette couche sensible aux infrarouges est une couche d'enregistrement à polymérisation par radicaux de type négatif ; qui est laminée séquentiellement.

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3. Plaque d'impression planographique selon la revendication 1, dans laquelle la conductivité thermique du matériau calorifuge est de 1,0 ( $\text{Wm}^{-1}\text{K}^{-1}$ ) ou moins.

4. Plaque d'impression planographique selon la revendication 2, dans laquelle la conductivité thermique du matériau calorifuge est de 1,0 ( $\text{Wm}^{-1}\text{K}^{-1}$ ) ou moins.

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5. Plaque d'impression planographique selon la revendication 1, dans laquelle le matériau calorifuge est une couche hydrophile réticulée.

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6. Plaque d'impression planographique selon la revendication 5, dans laquelle le matériau calorifuge comprend en outre un adhésif.

7. Plaque d'impression planographique selon la revendication 5, dans laquelle la plaque d'impression planographique comprend une couche adhésive entre la première couche et la deuxième couche.

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8. Plaque d'impression planographique selon la revendication 5, dans laquelle l'adhésivité du matériau calorifuge est améliorée en régulant l'équilibre entre le caractère hydrophobe et le caractère hydrophile du matériau calorifuge.

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9. Plaque d'impression planographique selon la revendication 1, dans laquelle la couche d'enregistrement à polymérisation par radicaux comprend un absorbeur d'infrarouges.

10. Plaque d'impression planographique selon la revendication 2, dans laquelle la couche d'enregistrement à polymérisation par radicaux comprend un absorbeur d'infrarouges.

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**11.** Plaque d'impression planographique selon la revendication 9, dans laquelle l'absorbeur d'infrarouges est l'un parmi un absorbeur d'infrarouges possédant une structure de sel d'onium et un absorbeur d'infrarouges anionique.

**12.** Plaque d'impression planographique selon la revendication 10, dans laquelle l'absorbeur d'infrarouges est l'un  
5 parmi un absorbeur d'infrarouges possédant une structure de sel d'onium et un absorbeur d'infrarouges anionique.

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